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RESEARCH ARTICLE

# Heavy Metal Evaluation of Overused Commercial Fertilizers and Their Interactions with Soil Properties

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**ABSTRACT**

Şanlıurfa province has 36% of the agricultural areas in Turkey and 64.1% of the agricultural areas in the GAP Region. With approximately 600 000 tons of chemical fertilizer consumption in 2021, it is the province with the most fertilizer consumption in Turkey. This causes some negative and high environmental risks such as salinization in the soil, heavy metal (HM) accumulation, deterioration of nutrient balance, damage to microorganism activity, and formation of eutrophication in the region. The objective of this study was to determine the HMs (Zn, Ni, Mn, Cu, Mo, Pb, Cd) concentrations of the soils and some commercial fertilizers overused, and evaluate their interactions with soil properties. The average values of HM concentration of the soil are as follows; 32.65 and 46.88 mg $kg^{-1}$ Zn; 649.03 and 730.58 mg $kg^{-1}$ Mn; 79.86 and 95.54 mg $kg^{-1}$ Ni; 0.15 to 0.27 mg $kg^{-1}$ Cd; 0.26 and 0.97 mg $kg^{-1}$ Mo; 8.54 and 18.67 mg $kg^{-1}$ Pb; 19.45-25.37 mg $kg^{-1}$ Cu. HM contents of some fertilizers were found to be very high in this study. This causes an increase in the HM concentration in the soil. HMs concentrations of several soil samples exceeded the threshold level of Europe standards except for Ni, Mo, and Mn. Study results can help the authorities to develop effective fertilizer management strategies for the Harran Plain, which has once again revealed the necessity of applying agricultural activities such as fertilization with a fertilization program prepared under expert control according to the results of soil analysis.

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## Introduction

The capital of the Southeastern Anatolia Project (GAP), one of the largest projects in the world, is Şanlıurfa. Şanlıurfa and Harran Plains is a large region covering an area of approximately 1,500 km². Within the scope of the GAP project, irrigated agriculture started in 1995 with the transmission of water to the plain through the Atatürk Dam Şanlıurfa Tunnels. In this way, plants such as cotton and corn, which need more water, have begun to be grown. Plant nutrient needs of these plants with high yield potential, which are grown in direct proportion to the increasing water need, have also increased and fertilizer usage habits have started to meet this need. Agricultural production and yield increased significantly in the plain. Since the fertilizer preference of the producers, for whom the fertilizer usage habits of the region are not directly dependent on the fertilizer type, were determined only based on price, the producer using a single type of fertilizer in the region could not be determined. Di-ammonium phosphate (DAP-18N:46$P_2O_5$), composite (20N:20$P_2O_5$:20$K_2O$, 15N:15$P_2O_5$:15$K_2O$, and 15N:15$P_2O_5$:15$K_2O$+Zn), ammonium nitrate (26%N, 33%N), ammonium sulfate (21%N), calcium ammonium nitrate (CAN-26%N) and urea (46%N) fertilizers are used extensively in the Harran Plain.

Irrigation of these plains, which constitute the largest arable and arable land of the GAP Region, is one of the most important components of the GAP in terms of regional development and

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high agricultural production potential (Güven & Taşlıgil, 2013). Irrigation in the region is in the form of surface irrigation. Due to this irrigation habit, the soils of the region faced the problem of salinization with the effect of clay texture. The main clay mineral of the Harran Plain soil is smectite, and the remaining clay minerals are palygorskite, chlorite, illite, and kaolinite. The high smectite content of the soil indicates that the soils are difficult to cultivate and will become alkaline with increasing $Na^+$ ions over time. Unplanned and unconscious irrigation, fertilization, and salinization in the region pose a great risk to sustainable agriculture (Seyrek et al., 2005).

Harran Plain has intensive agricultural production, increasing population and increasing food consumption depending on this population. For this reason, excessive commercial fertilizers are used in agricultural activities in this region. According to the province-based fertilizer consumption results of the Ministry of Agriculture, while 319,962 tons of fertilizer was consumed in Şanlıurfa in 2010, it was reported as 406,604 tons in 2015, 591,326 tons in 2020 and 597,376 tons in 2021. As a result, fertilizer consumption is increasing day by day. The increase in the chemical fertilizers used in agriculture has many negative effects on the environment and soil. Some of those; salinization in soil, deterioration of nutrient balance, damage to microorganism activity, nitrate accumulation in water and formation of eutrophication cause soil erosion, chemical fertilizers mix with water and increase the amount of phosphate in rivers, streams and lakes (İ. Sönmez et al., 2008; Liu & Lal, 2015).

The population growth rate in developed countries is 5 times lower than in developing countries. To meet the needs of the growing population in developing countries, little attention is paid to events such as environmental pollution and security that may have an impact after a long time, and they become quite commonplace (Atılgan et al., 2007). One of them is the damage to the environment of increased uncontrolled fertilizer consumption. Soil pollution must be prevented to hinder the deterioration of public health owing to the food and product chain in the future. This situation may create a serious food safety problem years later. The increasing use of chemical fertilizers (especially the use of high amounts) has come to endanger public health. It is also known that the useful living communities in the soil are naturally adversely affected by the chemicals used, as the quality of life of the plants decreases, and even the life of the plants.

The application time and amount of fertilizer applied to the soil affect plant yield and quality. The chemical fertilizers used in increased doses causes the accumulation of harmful and toxic substances in plants (Kara, 2005; Arora et al., 2008; Derin, 2019). The effects of HM accumulation on living organisms and soil can be short-term or long-term, so it is necessary to follow the accumulation closely, and to do the fertilizer dose amount and timing well (Sabiha-Javied et al., 2009; Derin, 2019).

Recently, commercial fertilizers used for agricultural purposes combine with some compounds and elements and accumulate in the soil so much that it adversely affects plant production. Agricultural activities carried out to increase the quality to provide the continuity of plant production and the product are very closely related. Some activities and practices can change soil properties (Kadıoğlu & Canbolat, 2014).

Micronutrients such as iron (Fe), manganese (Mn), zinc (Zn) and copper (Cu) are essential metals for plant yield and, most importantly, growth. But plants can accumulate heavy metals (HMs) or non-essential metals such as lead (Pb), nickel (Ni) and chromium (Cr) in the soil and can cause serious environmental problems (Mitsios et al., 2005). The HM concentration in the soil solution is important and plays a critical role for check the availability of the ions to plants (Lorenz et al., 1994). The bioavailability and solubility of HM ions vary greatly as many factors influence their concentration in the soil solution. The metal solubility or availability is affected by some factors such as soil pH (Sanders et al., 1987), organic matter content and clay content (Mitsios et al., 2005).

Recently, commercial fertilizers used for agricultural purposes combine with some compounds and elements and accumulate in the soil so much that it adversely affects plant production. Agricultural activities carried out to increase the quality to provide the continuity of plant production and the product are very closely related. Some activities and practices such as fertilization of the soil can change the soil properties (Kadıoğlu & Canbolat, 2014). The objective of this study were to (1): determine HMs (Zn, Ni, Mn, Cu, Mo, Pb, Cd) concentrations of the soils and some commercial fertilizers overused in the plain and (2): evaluate their interactions with soil properties in the plain.

## Materials and Methods

### *Site Descriptions*

The location of the study area (Harran Plain) was given in Figure 1. Harran Plain is in the southeastern province of Şanlıurfa, which is at the center of Turkey's largest irrigation and development project (GAP). It is located between 38°39'-39°30' East longitudes and 36°43'-37°11' North latitudes (mean elevation: 415 m) and covers an area of 225,000 ha.

Although 25 soil series were determined in the Harran plain, 6 of them are common in the study area. 21 of these series are clayey, two are clayey silt and the other is clayey loam texture. The predominant silicate clay mineral is smectite group clays, and palygorskite clay mineral is also found to be important. Although the lime content of its soils with an A-B-C horizon is high, the organic matter content is generally around 1% (DSİ, 2003; Büyükkılıç, 2009).

According to climate data, the annual average temperature in the Harran Plain is 16.1 ºC, the annual average precipitation is 365 mm and evaporation is 1 848 mm (MGM, 2021). It is known that its climate is arid and semi-arid, and the lack of water is excessive during most of the year (Akış et al., 2005; M. E. Sönmez, 2012).

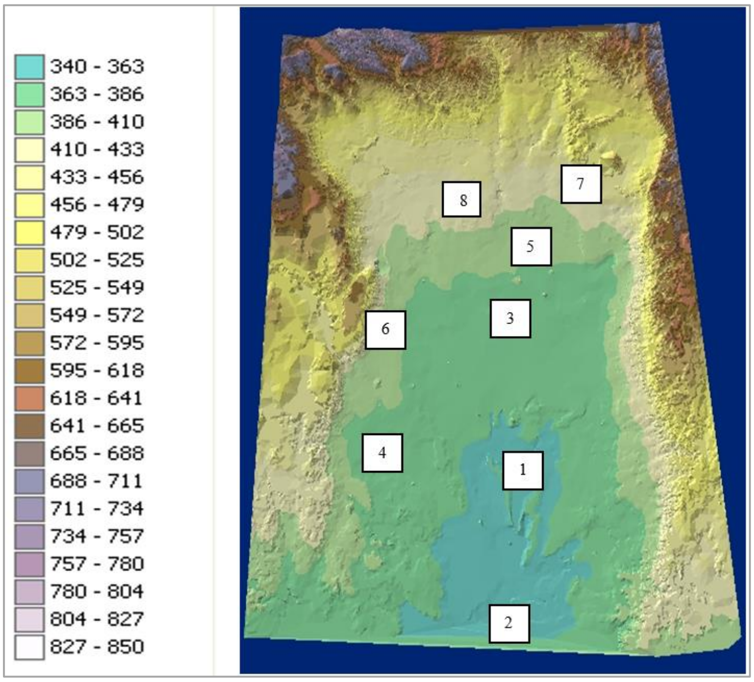


**Figure 1.** The location points of the studied soil.

### *Soil and Commercial Fertilizers Sampling*

Total samples from soil profiles were taken related to soil series from the genetic horizon (Table 1). Soil profiles (8 soil samples) were selected from different locations of the Harran Plain, which were grouped into 4 zone (Z) related to the elevation in the south, middle and north zones in the studied area. Zones identification and soil series in the Harran Plain were given in Table 1. Soil samples were taken from the soil surface horizon (approximately 0-30 cm) and subsurface horizon (approximately 30-60 cm) with three replicates, which were air-dried, ground, sieved to pass a 2-mm mesh and then stored in plastic bags for laboratory analyses.

**Table 1.** Zones identification and soil series in the study area.

| Zone Code | Profile Code | Series name | Coordinates |
|---|---|---|---|
| **Z1** | 1. | Çekçek | 36º56'49.9"N 38º54'05.8"E |
| | 2. | Kısas 2 | 36º58'05.6"N 39º01'09.5"E |
| **Z2** | 3. | Bellitaş | 37º01'09.6"N 39º09'13.2"E |
| | 4. | İkizce | 37º01'50.1"N 39º07'29.9"E |
| **Z3** | 5. | Sırrın | 37º05'46.1"N 39º02'14.4"E |
| | 6. | Beğdeş | 36º50'49.1"N 38º54'16.9"E |
| **Z4** | 7. | Gürgelen 2 | 36º47'13.6"N 39º05'25.8"E |
| | 8. | Akçakale | 36º45'37.0"N 39º58'53.8"E |

Universal Transverse Mercator (UTM): 37.

Some commercial fertilizer samples were purchased from various markets in Şanlıurfa city of Turkey, which are overused in the plain. 16 overused commercial fertilizers including 5 samples of diammonium phosphate (DAP, 18% N: 46% $P_2O_5$); 4 samples of composite 20:20 (20% N: 20% $P_2O_5$), one sample of composite 5 (15% N: 15% $P_2O_5$: 15% $K_2O$), one sample of composite 6 (15% N: 15% $P_2O_5$ + Zn); one sample of ammonium nitrate 1 (26% N), one sample of ammonium nitrate 2 (33% N), one sample of calcium ammonium nitrate (CAN; 26% N), one sample of ammonium sulfate (21% N), and one sample of urea (46% N) were selected according to the most consumed varieties in the plain. The collected samples were ground for analysis, and kept in plastic bags before laboratory analyses.

### *Chemical and Statistical Analysis*

The analysis was determined as follows: pH measured in a 1:1 water soil ratio solution according to Peech (1965)'s method; soluble salts according to Bower and Wilcox (1965); $CaCO_3$ according to Schribler calcimetric method; organic carbon according to Duchaufour (1970), cation exchange capacity following the method of Chapman (1965). Soil and fertilizers samples were digested by microwave and concentrations of HMs (Zn, Ni, Mn, Cu, Mo, Pb, Cd) were determined using an Agilent 7500a model of ICP-MS (Inductively Coupled Plasma Mass Spectrometer) and also atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer).

All data were analyzed by parametric multifactor analysis of variance (ANOVAs) and if need nonparametric test using the software package "SPSS Version 19.0" since the interaction between factors and processes was significant differences between soils/plants for selected subsets of data. The separation of means was made according to Tukey's verified significant difference at $p<0.05$. Relationships among properties were studied using Pearson correlations. Descriptive statistics (mean, median, standard deviation and range) of soil and properties were performed applying the Excel for Windows software package.

## Results and Discussion

### *Soil Properties and Total Heavy Metal Contents of Soil*

Soil characteristics of the studied area were given separately (surface and subsurface horizon) in Table 2. The clay contents were predominant, which varied between 28.5 and 57.8% in the surface, 27.1 and 65.7% in the subsurface horizons. The pH values ranged from 7.14 and 8.52 in the surface and 7.28 and 8.45 in the subsurface horizons. The soil salinity was high in some profiles, especially in Z1 due to excessive irrigation and high clay content. Soil organic matter contents were between 0.97 and 2.76% in the surface, and between 0.70 and 2.02% in the subsurface horizons. Lime contents were changed between 15.59 and 37.41% in the surface, and between 14.03 and 38.19% in the subsurface horizons. Cation exchangeable capacities were very high in some profiles (Table 2).

**Table 2.** Selected properties of the surface soils and subsurface horizons in the soil studied (n= 8 profiles).

| Parameter | Unit | Surface Horizon | | | Subsurface Horizon | | |
|---|---|---|---|---|---|---|---|
| | | *Max.* | *Min.* | *Mean* | *Max.* | *Min.* | *Mean* |
| **pH** | - | 8.52 | 7.14 | 7.98 | 8.45 | 7.28 | 7.98 |
| **EC** | dS $m^{-1}$ | 15.92 | 0.19 | 2.88 | 15.62 | 0.44 | 1.94 |
| **$CaCO_3$** | % | 37.41 | 15.59 | 26.35 | 38.19 | 14.03 | 26.84 |
| **OM** | % | 2.76 | 0.97 | 1.45 | 2.02 | 0.70 | 1.36 |
| **CEC** | $cmol^{(+)}$ $kg^{-1}$ | 49.22 | 28.78 | 38.89 | 48.76 | 28.44 | 37.28 |
| **Clay** | % | 57.80 | 28.50 | 46.96 | 65.70 | 27.10 | 51.16 |

EC: Electrical conductivity, OM: Organic matter, $CaCO_3$: Lime contents, CEC: Cation exchangable capacity.

Heavy metal concentrations were given in Table 3. The average values of HM concentration of the soil are as follows: 32.65 and 46.88 mg $kg^{-1}$ Zn; 649.03 and 730.58 mg $kg^{-1}$ Mn; 79.86 and 95.54 mg $kg^{-1}$ Ni; 0.15 to 0.27 mg $kg^{-1}$ Cd; 0.26 and 0.97 mg $kg^{-1}$ Mo; 8.54 and 18.67 mg $kg^{-1}$ Pb; 19.45-25.37 mg $kg^{-1}$ Cu. The heavy metal concentrations in zones were Z4>Z3>Z1>Z2, respectively (Table 3). There were statistically significant relations in the surface horizon between Zn and Ni, Cd; Ni and Cd in Z1, between Zn and Ni in the Z2, between Ni and Cd in the Z3, between Mo and Cd in Z4. In the subsurface horizon, statistically, the correlation was shown in the Z1, between Mo and Cd in the Z2, Zn and Mo in the Z3, and Ni and Cu in Z4. As a result of the analysis of variance (Two-way ANOVA), it was seen that the interaction of soil depth, zone and depth x zone of all heavy metals except Mo was not significant. On the other hand, statistical differences were observed with Mo in the interaction of zone and zone x depth ($p<0.05$).

The international threshold level of some HMs in the soil were given in Table 4. Concentrations of several soil samples exceeded the permissible limits of Europe standards except for Ni, Mo, and Mn contents of the soil. Zinc is an active biochemical process and is also known to be involved in various biological and chemical interactions with various elements in the soil. The mean average of Zn for world soils is 64 ppm and Zn concentration changes between 10 and 300 mg $kg^{-1}$ in agricultural soils (Kabata-Pendias & Pendias, 2001). In our study, Zn concentrations are lower than the maximum permissible limit; similar results are found by Kabata-Pendias and Pendias (2001) in agricultural soils. The mean average of Mn for world soils is 437 ppm, while for the U.S. soils is 495 ppm. Mn contents of the studied soil were higher than permissible limits. In this study, the Mn content of the soil was higher than the standard concentration of other authors (Kabata-Pendias & Pendias, 1992), one reason for this result can be the high HM contents of some applied fertilizers to plain.

**Table 3.** Heavy metals concentrations in the soil.

| Depth | Zone | Zn | Mn | Ni | Cd | Mo | Pb | Cu |
|---|---|---|---|---|---|---|---|---|
| Surface | 1 | 32.65 ± 4.91 | 730.58 ± 120.12 | 84.27 ± 12.85 | 0.15 ± 0.10 | 0.30 ± 0.35 | 11.98 ± 2.95 | 19.45 ± 2.64 |
| | 2 | 33.09 ± 10.04 | 651.82 ± 235.91 | 79.86 ± 15.90 | 0.17 ± 0.08 | 0.26 ± 0.15 | 14.34 ± 1.37 | 19.69 ± 2.74 |
| | 3 | 43.70 ± 11.68 | 649.03 ± 212.85 | 90.33 ± 5.80 | 0.20 ± 0.15 | 0.57 ± 0.11 | 11.73 ± 5.66 | 23.90 ± 1.75 |
| | 4 | 46.88 ± 17.51 | 670.99 ± 94.91 | 91.31 ± 2.75 | 0.27 ± 0.21 | 0.98 ± 0.73 | 8.54 ± 3.30 | 20.78 ± 1.10 |
| Subsurface | 1 | 41.74 ± 17.86 | 620.18 ± 132.13 | 87.27 ± 15.99 | 0.22 ± 0.20 | 0.53 ± 0.08 | 11.44 ± 2.36 | 20.32 ± 3.30 |
| | 2 | 40.62 ± 1.26 | 691.51 ± 159.40 | 89.91 ± 7.58 | 0.20 ± 0.07 | 0.33 ± 0.07 | 14.62 ± 0.32 | 21.46 ± 0.61 |
| | 3 | 41.86 ± 5.37 | 661.65 ± 125.82 | 95.54 ± 5.22 | 0.24 ± 0.10 | 0.40 ± 0.16 | 18.67 ± 3.54 | 25.37 ± 1.74 |
| | 4 | 39.00 ± 9.21 | 698.19 ± 166.19 | 88.66 ± 9.91 | 0.27 ± 0.12 | 0.49 ± 0.04 | 11.80 ± 4.43 | 20.79 ± 2.84 |
| **Two-way ANOVA Analysis** | | | | | | | | |
| **Depth** | | 0.42 ns | 0.13 ns | 0.95 ns | 0.69 ns | 0.74 ns | 1.56 ns | 0.91 ns |
| **Zone** | | 1.25 ns | 0.04 ns | 1.13 ns | 1.28 ns | 2.18 * | 0.55 ns | 1.34 ns |
| **Depth x Zone** | | 1.62 ns | 0.72 ns | 0.60 ns | 0.44 ns | 2.29 * | 1.27 ns | 0.28 ns |

*p<0.05, **p<0.01, ns: Not significant.

**Table 4.** The international threshold level of some HMs in the soil (mg kg$^{-1}$).

| Heavy Metals | EU | USA | Canada | UK | Turkey* |
|---|---|---|---|---|---|
| **Zn** | 300 | 200-300 | 1400 | 200 | 47 |
| **Cu** | 140 | 80-200 | 170 | 63 | 20 |
| **Pb** | 300 | 300 | 150 | 70 | 10 |
| **Cd** | 3.0 | 3.0 | 79.5 | 1.4 | 0.2 |
| **Ni** | 75 | 50-110 | 210 | 50 | 90 |
| **Mo** | 0.5 | | | | 0.6 |
| **Mn** | 437** | | | | 670 |

Source: CCME (2001), *Turkey (This study, 2022), **Kabata-Pendias (2001).

Likely, the soils of arid and semi-arid regions often have high Ni content. The grand mean for world soils is calculated to be 22 ppm, and 19 ppm was reported for U.S. soils. Likely that the soils of arid and semi-arid regions often have high Ni content. (Schacklette & Boerngen, 1984). Ni content changes between 1 and 100 mg kg$^{-1}$ (Kabata-Pendias & Pendias, 2001) in agricultural soil. Some samples were higher than the standards in the study areas. The Cu content of agricultural soils change between 5 and 50 mg kg$^{-1}$, which the concentrations below 8 mg kg$^{-1}$ may indicate a deficiency for some crops as Cu is an essential micronutrient (Mermut et al., 1996). The results of the study showed that all samples had normal range of Cu concentration in the agricultural soils of Harran Plain.

Soils in arid and semiarid regions, generally have higher Mo contents (Kabata-Pendias & Pendias, 1992). In this study, some results of Mo were slightly high the permissible limit. Evaluation of Pb levels in soils that are toxic to plants is not easy; however, several authors have produced results for very similar concentrations ranging from 100 to 500 ppm (Kabata-Pendias & Pendias, 2001). The results of Pb in soils were less than the permissible limit in this study. Recently, Pb concentrations in soils have increased day by day, and this situation can seriously inhibit microbial processes. All these effects should be expected mainly in soils with low CEC. Whereas, in the long run, they can also occur in other soils with higher CECs (McBride & Spiers, 2001).

### *Relationship between Soil Heavy Metal Concentrations and Some Soil Properties*

The trace element migration rates in the soil profiles are influenced by physical, chemical, and biological soil properties of which the most important are the Eh-pH system, CEC, salt content, amount and quality of organic matter, plant species, temperature and water, soil conditions such as pH and texture play a very important role in the availability of HMs in the soil (Öborn et al., 1995; Mermut et al., 1996; Puschenreiter & Horak, 2000). Correlation analysis was used to set up relationships between total concentrations of HMs and soil properties, which are given in Table 5. The CECs reflected the organic C and clay contents of the soils studied. Heavy metals (HMs) contents were affected by pH, CEC, Ca, $CaCO_3$, and clay contents in the surface horizon and by $CaCO_3$, CEC, and CEC in the subsurface horizons. The correlation coefficients analyses showed that there were positively relations between Zn and pH; Mn and CEC; Ca and Cu; Mo and $CaCO_3$; Pb and Clay in the surface horizons. On the contrary, total Zn, Ni, and Mo contents were negatively correlated with $CaCO_3$, CEC, and CEC in the subsurface horizons. Salinity, pH, organic matter, lime and clay contents were influenced the uptake of HMs in the soil (Grant et al., 2002).

**Table 5.** Correlation coefficients between soil parameters and total concentration of heavy metals.

| Soil Properties | | Heavy Metal Concentration | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | **Zn** | **Mn** | **Ni** | **Cu** | **Mo** | **Pb** | **Cd** |
| **Surface Horizon** | **pH** | 0.506* | -0.206 | 0.445 | 0.288 | 0.201 | -0.09 | 0.138 |
| | **EC** | -0.323 | 0.457 | -0.418 | -0.495 | -0.287 | 0.212 | -0.319 |
| | **$CaCO_3$** | 0.110 | -0.398 | -0.353 | -0.197 | 0.546* | -0.227 | 0.408 |
| | **SOC** | -0.238 | -0.081 | -0.427 | -0.404 | -0.172 | -0.168 | -0.205 |
| | **Ca** | 0.158 | 0.334 | 0.185 | 0.517* | -0.249 | 0.219 | 0.045 |
| | **K** | -0.267 | 0.434 | 0.269 | 0.218 | -0.437 | 0.326 | -0.020 |
| | **Mg** | 0.238 | -0.189 | 0.406 | 0.473 | -0.016 | -0.274 | -0.078 |
| | **Na** | -0.153 | 0.483 | -0.218 | -0.343 | -0.054 | -0.012 | -0.172 |
| | **CEC** | 0.123 | 0.550* | 0.090 | 0.236 | -0.348 | 0.288 | -0.065 |
| | **Clay** | -0.336 | -0.262 | 0.080 | -0.016 | -0.425 | 0.514* | -0.188 |
| **Next to Surface Horizon** | **pH** | -0.157 | -0.219 | -0.007 | -0.015 | 0.051 | -0.154 | 0.143 |
| | **EC** | -0.017 | 0.073 | -0.357 | -0.262 | -0.183 | -0.118 | -0.217 |
| | **$CaCO_3$** | -0.530* | -0.384 | -0.439 | -0.242 | -0.263 | -0.341 | -0.146 |
| | **SOC** | -0.085 | 0.104 | -0.071 | -0.016 | -0.043 | 0.320 | -0.218 |
| | **Ca** | -0.268 | 0.079 | -0.217 | 0.036 | -0.389 | 0.295 | -0.114 |
| | **K** | 0.104 | -0.046 | 0.201 | 0.099 | 0.244 | -0.212 | 0.334 |
| | **Mg** | 0.018 | -0.156 | 0.243 | 0.308 | 0.001 | 0.244 | 0.019 |
| | **Na** | -0.190 | 0.374 | -0.357 | -0.488 | -0.148 | -0.359 | 0.123 |
| | **CEC** | -0.432 | 0.148 | 0,529* | -0.368 | -0.547* | -0.051 | -0.183 |
| | **Clay** | 0.269 | -0.079 | 0.216 | 0.118 | 0.333 | 0.151 | 0.015 |

* Correlation is significant at the 0.05 level (p), ** Correlation is significant at the 0.01 level (p).

Zone 2 (Z2) had high pH, low salinity, low organic matter, high calcium carbonate, and also high clay contents; this is the reason for the low HM concentration in Z2. The concentrations of HMs were in the following order Z4>Z3>Z1>Z2 in the studied area. Interactions between clays and metals in soil regulate plant availability of metals required for the growth of crops, while also soils contain a complex mix of clay, organic matter, coarse particles, water, air, and biological entities with properties that change both in space and over time. Therefore, it is not easy to accurately predict the chemical reactions and long-term travel of metals in a given soil (Hesterberg, 2006). All concentrations of several soil samples exceeded the permissible limits of Europe standard except for Ni, Mo, and Mn.

Soil pH is controlled by the availability of toxic elements to plants in the soil. The bioavailability of Zn and Cu is mainly controlled by pH and organic carbon content (Bhogal et al., 2003) Low Mn solubility was found at neutral to alkaline pH. CEC played an important role in the sorption of Cd in soils. Schuman (1979) also found that HMs in soil were associated primarily with clay fraction. Similarly, positive correlations between total HM contents and clay contents of soils were found in Oklahoma Benchmark soils (Lee et al., 1997). McBride and Spiers (2001) indicated that soils with HMs contamination are dependent on the soil location, source of fertilizer source, and soil organic matter.

### *Total Heavy Metal Contents in Commercial Fertilizers*

The heavy metal (HM) contents of some commercial di-ammonium-phosphate (DAP) fertilizers were given in Table 6. Accordingly, Cu content was 28.29 mg $kg^{-1}$ in DAP 4, Zn content was highest 183.84 mg $kg^{-1}$ in DAP 2 and 305.84 mg $kg^{-1}$ in DAP 4, Pb and Mo content was high 9.12 mg $kg^{-1}$, 7.94 mg $kg^{-1}$ in DAP 1, Ni content was high 13.20 mg $kg^{-1}$ in DAP 1 and 27.62 mg $kg^{-1}$ in DAP 4, Mn content was high 193.99 mg $kg^{-1}$ in DAP 1 and 67.95 mg $kg^{-1}$ in DAP 4, and Cd content was high 17.16 mg $kg^{-1}$ in DAP 2 and 18.10 mg $kg^{-1}$ in DAP 3.

**Table 6.** Heavy metal contents of various di-ammonium-phosphate (DAP) fertilizers used in Harran Plain.

| Fertilizers | Contents | Cu | Zn | Pb | Mo | Ni | Mn | Cd |
|---|---|---|---|---|---|---|---|---|
| | | mg kg$^{-1}$ | | | | | | |
| **DAP 1** | 18N:46$P_2O_5$ | 0.01 | 45.34 | 9.12 | 7.94 | 13.20 | 193.99 | 3.52 |
| **DAP 2** | 18N:46$P_2O_5$ | 0.00 | 183.84 | 1.75 | 3.41 | 10.37 | 24.56 | 17.16 |
| **DAP 3** | 18N:46$P_2O_5$ | 0.37 | 109.57 | 2.90 | 5.42 | 9.16 | 24.84 | 18.10 |
| **DAP 4** | 18N:46$P_2O_5$ | 28.29 | 305.84 | 3.59 | 4.73 | 27.62 | 67.95 | 7.52 |
| **DAP 5** | 18N:46$P_2O_5$ | 0.50 | 102.40 | 0.88 | 4.93 | 11.35 | 25.78 | 10.52 |

Heavy metal contents in composite fertilizers were given in Table 7. Accordingly, Cu contents was high 15.95 mg kg$^{-1}$ in composite 3 and 15.46 mg kg$^{-1}$ in composite 4, Zn and Pb content was very high 8813.99 mg kg$^{-1}$, 175.14 mg kg$^{-1}$ in composite 3 and 3021.12 mg kg$^{-1}$, 130.62 mg kg$^{-1}$ in composite 6, Mo content was high 3.73 mg kg$^{-1}$ in composite 6 and 2.79 mg kg$^{-1}$ in composite 2, Ni content was high 16.93 mg kg$^{-1}$ in composite 1 and 22.03 mg kg$^{-1}$ in composite 3. Mn content was found to be high 54.72 mg kg$^{-1}$ in composite 3 and 119.12 mg kg$^{-1}$ in composite 5, while the Cd content was high 7.75 mg kg$^{-1}$ in composite 2 and 6.37 mg kg$^{-1}$ in composite 4.

**Table 7.** Heavy metal contents of various composite fertilizers used in Harran Plain.

| Fertilizers | Contents | Cu | Zn | Pb | Mo | Ni | Mn | Cd |
|---|---|---|---|---|---|---|---|---|
| | | mg kg$^{-1}$ | | | | | | |
| **Composite 1** | 20N:20$P_2O_5$ | 4.39 | 682.73 | 16.50 | 0.72 | 16.93 | 17.27 | 3.76 |
| **Composite 2** | 20N:20$P_2O_5$ | 0.66 | 96.94 | 3.18 | 2.79 | 7.29 | 17.15 | 7.75 |
| **Composite 3** | 20N:20$P_2O_5$ | 15.95 | 8813.99 | 175.14 | 2.65 | 22.03 | 54.72 | 3.85 |
| **Composite 4** | 20N:20$P_2O_5$ | 15.46 | 133.29 | 1.69 | 1.41 | 13.49 | 7.90 | 6.37 |
| **Composite 5** | 15N:15$P_2O_5$:15$K_2O$ | 0.17 | 43.52 | 8.34 | 0.00 | 2.84 | 119.12 | 0.02 |
| **Composite 6** | 15N:15$P_2O_5$:15$K_2O$+Zn | 6.02 | 3021.12 | 130.62 | 3.73 | 6.21 | 15.22 | 8.92 |

The heavy metal content of some nitrogen fertilizers overused in the Harran Plain was given in Table 8. The results showed that Ni and Mn contents are high in ammonium nitrate 1 and CAN fertilizers. In this study, the HM content of some fertilizers was very high. This was one of the reasons for the high concentration of HMs in the soil (Ajayi et al., 2012; Büyükkılıç Yanardağ et al., 2016). Some commercial fertilizer types such as composite and DAP, which was overused in the plain, have higher HM contents. There was an important relationship between HMs and fertilizers. As it is known, land applications of commercial fertilizers can directly pollute the soil if it has high HM content.

Commercial fertilizers used in agriculture leave significant HMs to soils. The most important of these metals are arsenic, lead, cadmium, copper and nickel. Their entry into the soil is mostly done with phosphorus fertilizers and their raw materials. Research to produce phosphorus fertilizer has shown that the HM contents of phosphate rock are significantly high (especially imported from abroad). It has also been determined that the Cd and As content of phosphate rock is very high compared to other fertilizers (Köleli & Kantar, 2006).

**Table 8.** Heavy metal contents of some nitrogen fertilizers used in Harran Plain.

| Fertilizers | Contents | Cu | Zn | Pb | Mo | Ni | Mn | Cd |
|---|---|---|---|---|---|---|---|---|
| | | mg kg$^{-1}$ | | | | | | |
| **Ammonium Nitrate 1** | %26 N | 0.00 | 0.00 | 2.81 | 0.00 | 23.97 | 83.64 | 0.01 |
| **Ammonium Nitrate 2** | %33 N | 0.00 | 0.00 | 0.59 | 0.00 | 1.15 | 1.10 | 0.02 |
| **Ammonium Sulfate** | %21 N | 0.00 | 0.00 | 0.00 | 0.00 | 1.92 | 2.37 | 0.01 |
| **CAN** | %26 N | 0.00 | 1.39 | 3.03 | 0.00 | 32.84 | 97.90 | 0.00 |
| **Urea** | %46 N | 0.00 | 0.00 | 0.00 | 0.00 | 2.09 | 2.70 | 0.01 |

Fertilizer-metal standards valid in some countries in the world (Benson et al., 2014) were given in Table 9. Accordingly, fertilizers with high HM content were used in some countries. Although the maximum Pb, As, Cd, and Ni concentrations were determined as 11, 81, 114, and 201 mg $L^{-1}$ P, respectively, according to the volume principle of phosphoric acid in phosphorus fertilizers in fertilizer production, this ratio is the limit for lead concentration in composite fertilizers. It is approximately 5 times the value (100 mg $kg^{-1}$). Heavy metal, especially Cd content of DAP, TSP, and composite fertilizers used in agriculture to get more efficiency is high (>8 mg $kg^{-1}$ fertilizer) [Köleli & Kantar, 2006].

When we examined the different heavy metal of the same fertilizers; while Cu, Zn, Ni are more in DAP 4 fertilizer, Pb, Mo, Mn are more in DAP 1 fertilizer. Also, Cd content was more in DAP 1 fertilizer. When we examined the composite fertilizers; Cu ratio more in composite 3 and composite 4, Zn and Ni in composite 1 and composite 3, Mo in composite 3, Mn and Cd in composite 4. Ni and Mn are found to be very high in all nitrogen fertilizers except of CAN. Generally, phosphate fertilizers are produced from phosphate rocks by pickling. Sulfuric acid is used for pickling single superphosphate and phosphoric acid is used for pickling triple superphosphate. The results showed that due to the different heavy metal content of phosphate rocks used in fertilizer production, fertilizers with the same N:P content produced may have different heavy metal concentrations. The final product thus obtained contains all the heavy metals found as components in the phosphate rock (Mortvedt, 1996; Dissanayake & Chandrajith, 2009). Commercial inorganic fertilizers and especially phosphate fertilizers can potentially contribute to the global transport of heavy metals (Carnelo et al., 1997).

The increase in the HM ratio in the water and especially in the soil is very effective in soil fertility, aquatic life, and ecosystem activities. Metals enter the plant body and affect many important metabolic activities (Köleli & Kantar, 2006; Asri et al., 2007). In particular, fertilizers containing high sodium and potassium content reduce the deterioration of soil structure, and the soil pH, increased the properties of acidic irrigation or increased the benefits of other agricultural activities (Savci, 2012). Continuous use of acid-forming nitrogen fertilizers causes a decrease in soil pH, calcification, and a decrease in yield if not carried.

The basic use of fertilizers in the soil causes an increase in pH, and increases in the soil and plants, while its harmful effects can cause a sudden decrease in the pH of the seedlings and a decrease in yield and quality. In addition, they accumulate in the soil and cause soil pollution (Savci, 2012). When a large amount of potassium fertilizer is given to the soil, it disrupts the balance of Ca, Fe, and Zn and prevents nutrients from being taken up by plants. However, considering the negative effects on organisms, various earthworms and soil mites have devastating and lethal effects (Savci, 2012).

**Table 9.** Fertilizer-metal standards valid in some countries in the world (Benson et al., 2014).

| **Metal** | **China** | **Canada** | | | **Australia** | | | **Japan** |
|---|---|---|---|---|---|---|---|---|
| | F | MC | PF | PFM | PFC | FM | FNM | FP |
| **Cd** | 8 | 20 | 300 | 10 | 50 | - | - | 8 |
| **Cu** | - | - | - | - | - | - | - | - |
| **Ni** | - | 180 | - | - | - | - | - | - |
| **Pb** | 100 | 500 | - | - | - | - | 500 | 100 |
| **Zn** | - | 1850 | - | - | - | - | - | - |

F: mg $kg^{-1}$ fertilizer, MC: mg $kg^{-1}$ dw max. acceptable metal concentration, PF: mg $kg^{-1}$ P product P fertilizers, PFM: mg $kg^{-1}$ product P-free fertilizers, PFC: mg $kg^{-1}$ product fertilizers composed entirely of micronutrients, FM: mg $kg^{-1}$ all fertilizers and micronutrients, FNM: mg $kg^{-1}$ fertilizers with essential nutrients with micronutrients, FP: mg $kg^{-1}$ by-product phosphate fertilizers.

Soil properties affect the retention of some metals (Cd, Zn and Ni) during fertilizer application. Fertilized soils had significantly lower ($p<0.05$) levels of present and total metals than unfertilized soils, indicating that prolonged fertilization did not increase the metal concentration in the soil (Jones et al., 2002; Franklin et al., 2005). At concentrations of Cd, Mo, and As in high phosphorus fertilizers, agronomic application rates do not significantly increase total soil concentrations above background levels for many years, although their availability by plants for root uptake into tissues may increase (McBride & Spiers, 2001).

It is known that heavy metals occur in soil in various chemical forms - soluble in water, changeable but depending on certain regions of organic and inorganic components and in the structure of primary and secondary minerals with a balance between these forms (Mclaren & Crawford, 1993). This balance may change depending on the changes in physical, chemical and biological properties of the soil. Sims (1986) concluded that fertilizer application can not only provide nutrients to plants but also alter the speciation and bioavailability of HMs in soil.

## Conclusion

For the growing human population, increasing food production and improving soil quality has been a very important research topic. Especially with the use of commercial fertilizers with high metal content, serious soil pollution has occurred in agricultural lands. Toxic HM enters the food chain by passing it to the plant through fertilizers and then to the soil. Therefore, maximum tolerable limits for crops were determined by many countries. The soils in the plain are well developed and consist of A-B-C horizons, clay, carbonate contents, and CEC values are high; however, they have about 1% organic matter, low EC (non-saline) and classified as Vertisol. Total Fe contents in the majority of the surface soils are about 3%. The results of the study showed that HMs in soil zones were in the following order Z4>Z3>Z1>Z2. The reasons of those ratios were high pH, low salinity, low organic matter, high calcium carbonate, and also high clay contents. There were positively relations between Zn and pH; Mn and CEC; Ca and Cu; Mo and $CaCO_3$; Pb and Clay in the surface horizons. On the contrary, total Zn, Ni, and Mo contents were negatively correlated with $CaCO_3$, CEC, and CEC in the subsurface horizons. Although HM concentrations of common commercial fertilizers were lower than the standards, HM contents of some fertilizers were found to be very high in this study. This causes an increase in the HM concentration in the soil. HMs concentrations of several soil samples exceeded the threshold level of Europe standard except for Ni, Mo and Mn. Study results can help the authorities to develop effective fertilizer management strategies for the Harran Plain, which has once again revealed the necessity of applying agricultural activities such as fertilization with a fertilization program prepared under expert control according to the results of soil analysis.

## Conflict of Interest

The author has no conflict of interest to declare.

## References

Ajayi, S. O., Odesanya, B. O., Avwioroko, A. O., Adebambo, G. S., & Okafor, B. (2012). Effects of long-term fertilizer use on trace metal levels of soils in a farm settlement. *E3 Journal of Agricultural Research and Development*, *2*(2), 44-51.

Akış, A., Kaya, B., Seferov, R., & Başkan, H. O. (2005). Harran ovası ve çevresindeki tarım arazilerinde tuzluluk problemi ve bu problemin iklim özellikleriyle ilişkisi. *Selçuk Üniversitesi Sosyal Bilimler Enstitüsü Dergisi*, *14*, 21-38. (In Turkish)

Arora, M., Kiran, B., Rani, S., Rani, A., Kaur, B., & Mittal, N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. *Food Chemistry*, *111*(4), 811-815. https://doi.org/10.1016/j.foodchem.2008.04.049

Asri, F. Ö., Sönmez, S., & Çıtak, S. (2007). Kadmiyumun çevre ve insan sağlığı üzerine etkileri. *Derim Dergisi*, *24*(1), 34-41. (In Turkish)

Atılgan, A., Coşkan, A., Saltuk, B., & Erkan, M. (2007). Antalya yöresindeki seralarda kimyasal ve organik gübre kullanım düzeyleri ve olası çevre etkileri. *Ekoloji Dergisi*, *15*(62), 37-47. (In Turkish)

Benson, N. U., Anake, W. U., & Etesin, U. M. (2014). Trace metals levels in inorganic fertilizers commercially available in Nigeria. *Journal of Scientific Research & Reports*, *3*(4), 610-620.

Bhogal, A., Nicholson, F. A., Chambers, B. J., & Shepherd, M. A. (2003). Effects of past sewage sludge additions on heavy metal availability in light textured soils: Implications for crop yields and metal uptakes. *Environmental Pollution*, *121*(3), 413-423. https://doi.org/10.1016/s0269-7491(02)00230-0

Bower, C. A., & Wilcox, L. V. (1965). Soluble salts. In C. A. Black (Ed.), *Methods of soils analysis* (pp. 933-940). American Society of Agronomy.

Büyükkılıç, A. (2009). *Cadmium contents of soils and durum-bread wheats in Harran plain, SE Turkey* (Master’s thesis, Harran University). (In Turkish)

Büyükkılıç Yanardag, A., Mermut, A. R., Cano, Á. F., Garces, D. M. C., & Yanardağ, İ. H. (2016). Cadmium contents of soils and durum and bread wheats on Harran Plain, southeast Turkey. *Turkish Journal of Agriculture Forestry*, *40*, 772-782 https://doi.org/10.3906/tar-1602-95

Carnelo, L. G. L., de Miguez, S. R., & Marbán, L. (1997). Heavy metals input with phosphate fertilizers used in Argentina. *Science of the Total Environment*, *204*(3), 245-250. https://doi.org/10.1016/S0048-9697(97)00187-3

CCME (Canadian Council of Ministers for the Environment). (2001). *Canadian water quality guidelines for the protection of aquatic life*. https://ccme.ca/en/res/wqimanualen.pdf

Chapman, H. D. (1965). Cation exchange capacity. In C. A. Black (Ed.), *Methods of soil analysis* (pp. 891-900). American Society of Agronomy.

Derin, P. (2019). *Karaali (Şanlıurfa) jeotermal sahasının ağır metal kirliliği açısından araştırılması* (Master’s thesis, Harran University). (In Turkish)

Dissanayake, C. B., & Chandrajith, R. (2009). Phosphate mineral fertilizers, trace metals, and human health. *Journal of the National Science Foundation of Sri Lanka*, *37*(3), 153-165. https://doi.org/10.4038/jnsfsr.v37i3.1219

DSİ. (2003). *Problems of drainage and salinity in the Harran plain*. Summary Report, the 15th District Directorate of the State Hydraulic Works. (In Turkish)

Duchaufour, P. (1970). *Précis de pédologie*. Masson.

Franklin, R. E., Duis, L., Brown, R., & Kemp T. (2005). Trace element content of selected fertilizers and micronutrient source materials. *Communications of Soil Science and Plant Analysis*, *36*(11-12), 1591-1609. https://doi.org/10.1081/CSS-200059091

Grant, C. A., Bailey, L. D., Harapiak, J. T., & Flore N. A. (2002). Effect of phosphate source, rate and cadmium content and use of *Penicillium bilaii* on phosphorus, zinc and cadmium concentration in durum wheat grain, *Journal of the Science of Food and Agriculture*, *82*(3), 301-308. https://doi.org/10.1002/jsfa.1034

Güven, Ş., & Taşlıgil, N. (2013). Güneydoğu Anadolu Projesi (GAP)'nin dünü bugünü yarını. *Akademik Bakış Dergisi*, *36*, 1-26. (In Turkish)

Hesterberg, D. (2006). *Encyclopedia of soil science*. CRC Press. https://doi.org/10.1081/e-ess3

Jones, D. L., Campbell, G., & Kaspar, C. W. (2002). Human enteric pathogens. In: P. M. Haygarth & S. C. Jarvis (Eds.), *Agriculture, hydrology and water quality* (pp. 133-153). CABI Publishing.

Kabata-Pendias, A., & Pendias, H. (1992). *Trace elements in soils and plants*. CRC Press.

Kabata-Pendias, A., & Pendias, H. (2001). *Trace elements in soils and plants*. CRR Press.

Kadıoğlu, B., & Canbolat, M. Y. (2014). Toprak kalite indeks parametrelerinin tarım ve mera alanlarında farklı topoğrafik pozisyonlara bağlı olarak değişimi. *Alınteri Zirai Bilimler Dergisi*, *26*(1), 1-8. (In Turkish)

Kara, Y. (2005). Bioaccumulation of Cu, Zn and Ni from the wastewater by treated *Nasturtium officinale*. *International Journal of Environmental Science and Technology*, *2*(1), 63-67. https://doi.org/10.1007/BF03325859

Köleli, N., & Kantar, Ç. (2006). Fosforlu gübrelerde ağır metal tehlikesi. *Ekoloji Dergisi*, *9*, 1-5. (In Turkish)

Lee, B. D., Carter, B. J., Basta, N. T., & Weaver, B. (1997). Factors influencing metal distribution in six oklahoma benchmark soils. *Soil Science Society of America Journal*, *61*(1), 218-223. https://doi.org/10.2136/sssaj1997.03615995006100010030x

Liu, R., & Lal, R. (2015). Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions. *Science of the Total Environment*, *514*, 131-139. https://doi.org/10.1016/j.scitotenv.2015.01.104

Lorenz, S. E., Hamon, R. E., & McGrath, S. P. (1994). Differences between soil solutions obtained from rhizosphere and non-rhizosphere soils by water displacement and soil centrifugation. *European Journal of Soil Science*, *45*(4), 431-438. https://doi.org/10.1111/j.1365-2389.1994.tb00528.x

McBride, M., & Spiers, G. (2001). Trace element content of selected fertilizers and dairy manures as determined by ICP-MS. *Communications in Soil Science and Plant Analysis*, *32*(1-2), 139-156. https://doi.org/10.1081/CSS-100102999

Mclaren, R., & Crawford, D. V. (1993). Studies on soil copper I. The fractionation of copper in soils. *European Journal of Soil Science*, *24*(2), 172-181. https://doi.org/10.1111/j.1365-2389.1973.tb00753.x

Mermut, A. R., Jain, J. C., Li, S., Kerrich, R., Kozak, L., & Jana, S. (1996). Trace element concentrations of selected soils and fertilizers in Saskatchewan, Canada. *Journal of Environmental Quality*, *25*(4), 845-853. https://doi.org/10.2134/jeq1996.00472425002500040028x

MGM (Meteroloji Genel Müdürlüğü). (2021). *T.C. Çevre, Şehircilik ve İklim Değişikliği Bakanlığı, Meteoroloji Genel Müdürlüğü, 2021 verileri*. https://mgm.gov.tr/sondurum/toplam-yagis.aspx (In Turkish)

Mitsios, I. K., Golia, E. E., & Tsadilas, C. D. (2005). Heavy metal concentrations in soils and irrigation waters in Thessaly region, central Greece. *Communications in Soil Science and Plant Analysis*, *36*(4-6), 487-501. https://doi.org/10.1081/CSS-200043229

Mortvedt, J. J. (1996). Heavy metal contaminants in inorganic and organic fertilizers. In C. Rodriguez-Barrueco (Ed.), *Fertilizers and environment* (pp. 5-11). Springer.

Öborn, I., Jansson, G., & Johnsson, J. (1995). A field study on the influence of soil pH on trace element levels in spring wheat (*Triticum aestivum*), potatoes (*Solanum tuberosum*) and carrots (*Daucus carota*). *Water, Air, and Soil Pollution*, *85*, 835-840. https://doi.org/10.1007/BF00476933

Peech, M. (1965). Hydrogen-ion. In C. A. Black (Ed.), *Methods of soil analysis* (pp. 914-916). American Society of Agronomy.

Puschenreiter, M., & Horak, O. (2000). Influence of different soil parameters on transfer factor soil to plant of Cd, Cu and Zn for wheat and rye. *Die Bodenkultur*, *51*(1), 3-10.

Sabiha-Javied, M. T., Chaudhry, M. M. Tufai, M., & Irfan, N. (2009). Heavy metal pollution from phosphate rock used for the production of fertilizer in Pakistan. *Microchemical Journal*, *91*(1), 94-99. https://doi.org/10.1016/j.microc.2008.08.009

Sanders, J. R., McGrath, S. P., & Adams, T. (1987). Zinc, copper and nickel concentrations in soil extracts and crops grown on four soils treated with metalloaded sewage sludges. *Environmental Pollution*, *44*(3), 193-210. https://doi.org/10.1016/0269-7491(87)90003-0

Savci, S. (2012). Investigation of effect of chemical fertilizers on environment. *APCBEE Procedia*, *1*(2012), 287-292. https://doi.org/10.1016/j.apcbee.2012.03.047

Schacklette, H. T., & Boerngen, J. G. (1984). Element concentrations in soils and other surficial materials of the conterminous United States. *U.S. Geological Survey Proffessional Paper, 1270*, 1-10.

Schuman, L. M. (1979). Zinc, manganese and copper in soil fractions. *Soil Science*, *127*(1), 10-17. https://doi.org/10.1097/00010694-197901000-00002

Seyrek, A., Aydemir, S., & İnce, F. (2005). Harran ovasında tuzlulaşma eğilimi gösteren toprakların kil mineralojisi. *Atatürk Üniversitesi Ziraat Fakültesi Dergisi*, *36*(2), 137-144. (In Turkish)

Sims, J. T. (1986). Soil pH effects on the distribution and plant availability of manganese, copper and zinc. *Soil Science Society of America Journal*, *50*(2), 367-373. https://doi.org/10.2136/sssaj1986.03615995005000020023x

Sönmez, İ., Kaplan, M., & Sönmez, S. (2008). Kimyasal gübrelerin çevre kirliliği üzerine etkileri ve çözüm önerileri. *Batı Akdeniz Tarımsal Araştırma Enstitüsü Derim Dergisi*, *25*(2), 24-34. (In Turkish)

Sönmez, M. E. (2012). Barajların mekân üzerindeki olumsuz etkileri ve Türkiye'den örnekler. *Gaziantep Üniversitesi Sosyal Bilimler Dergisi*, *11*(1), 213-231. (In Turkish)