Hittite Journal of Science and Engineering, 2023, 10 (1) 49-56
ISSN NUMBER: 2148-4171
DOI: 10.17350/HJSE19030000290

Monitoring of Lead and Some Heavy Metals in Wheat Flour of Corum Province, Turkey: An Air Quality Comparison

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ABSTRACT

Food security is a priority issue for sustainable global development. Metal uptake by plants could have a significant impact on crop quality in areas of rapid industrialization with high fallout of airborne particles. In this study, concentrations of some heavy metals (copper, Cu; zinc, Zn; and lead, Pb) in flour samples supplied in Çorum, defined as one of the "New Industry Focus", were investigated using inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the heavy metal contamination. The results showed that the concentration of Pb in all samples examined exceeded the maximum permissible limit. To monitor the increase in Pb concentration and its relationship with air pollution, a two-year laboratory experiment was conducted. It was found that the increase in Pb concentration of about 47% and 77% for two flour samples was consistent with the increase in annual average particulate matter with diameter 10 micrometers PM_{10} concentrations (55% and 82%) obtained from two stations.

Keywords:
Wheat flour; Heavy metal; Lead; ICP-OES; Toxic elements; Nutrition; Bioindicator

Article History:
Received: 2022/11/19
Accepted: 2023/02/18
Online: 2023/03/31

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INTRODUCTION

Wheat is known and consumed as an important basic agricultural product all over the world. Wheat flour, bread, and various pastries obtained by processing wheat are foods offered for human consumption. Wheat, which is the raw material of these foods, has become indispensable for some basic food products. The presence of heavy metals in wheat flour due to enviromental pollution has raised substantial concerns about the possibility of toxic elements being transported to higher levels of the food chain, especially humans [1, 2]. For this reason, the content of toxic elements in cereals should be kept under control. The toxic mechanism of heavy metals functions in similar pathways, usually via reactive oxygen species (ROS) generation, enzyme inactivation, and suppression of the antioxidant defense. For example, the metals cadmium, nickel, chromium, and arsenic are known to inhibit DNA synthesis and repair mechanisms. Lead, a harmful environmental pollutant that has high toxic effects on many body organs, can induce neurological, respiratory, urinary, and cardiovascular disorders due to immunomodulation, oxidative, and inflammatory mechanisms [3, 4, 5]. The thresholds for certain toxic metals are presented in Table 1.

Crop production is highly dependent on environmental conditions and is particularly affected by air quality. Large quantities of heavy metals are released into the environment due to the rapid development of industry, traffic and transportation, and mining industry. Heavy metal-contaminated soil can lead to crop pollution through root accumulation and translocation. However, the uptake and root-to-shoot transport of highly toxic heavy metals that have no known function in plants, such as lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg), are restricted by the plant with different mechanisms to protect the aerial parts against these harmful heavy metals [6]. Therefore, air pollution poses a more significant threat in agricultural fields because heavy metals in the atmospheric particulate matter (PM, a mixture of solid particles and liquid droplets found in the air), known as PM1.0 (fine inhalable particles, with diameters that are generally 1.0 micrometers and smaller), PM2.5 (fine inhalable particles, with diameters that are generally 2.5 micrometers and smaller), and PM10 (inhalable particles, with diameters that are generally 10 micrometers and smaller), can directly en-

Table 1. The thresholds for certain toxic metals

Toxic metals	Compartment	Agency	Description	Limits
Chromium	Air	WHO	Air Quality Guidelines Chromium (VI)	1 μg/m³ for lifetime risk of 4×10^{-2}
	Workplace Air	OSHA	Legal limit over an 8-hour workday of Cr (VI)	0.005 mg/m³
		OSHA	Legal limit over an 8-hour workday of Cr (III)	0.5 mg/m³
		OSHA	Legal limit over an 8-hour workday of Cr (0)	1 mg/m³
	Drinking water	WHO	Drinking-Water Quality Guidelines for total chromium	0.05 mg/L
		EPA	Maximum contaminant level for total chromium	0.1 mg/L
	Bottled Water	FDA	Not to exceed the total chromium concentration	0.1 mg/L
Nickel	Air	WHO	Air Quality Guidelines	3.8×10^{-4} μg/m³
	Workplace Air	OSHA	Legal limit over an 8-hour workday of Ni in air	1 mg/m³
	Drinking water	WHO	Drinking-Water Quality Guidelines	0.02 mg/L
		EPA	Drinking water threshold	0.1 mg/L
Arsenic	Air	WHO	Air Quality Guidelines	1.5×10^{-3} μg/m³
		WHO	Air Quality Guidelines for estimation of cancer risk for a lifetime exposure	1 μg/m³
	Workplace Air	OSHA	Legal limit over an 8-hour workday of airborne arsenic in places that use inorganic arsenic	10 μg/m³
	Drinking Water	WHO	Drinking water threshold	0.01 mg/L
		EPA	Drinking water threshold	0.05 mg/L
Cadmium	Air	WHO	Air Quality Guidelines	5 ng/m³
	Workplace Air	OSHA	Legal limit over an 8-hour workday of cadmium in air	5 μg/m³
	Drinking Water	EPA	Drinking water at this concentration for a lifetime exposure does not cause adverse effects	0.005 mg/L
		WHO	Drinking water Quality Guidelines	0.003 mg/L
	Bottled Water	FDA	Bottled water threshold	0.005 mg/L
Lead	Air	WHO	Air Quality Guidelines	No Data
	Workplace Air	OSHA	Legal limit over an 8-hour workday in general industry for elemental, organic and inorganic lead	0.5 mg/m³
	Drinking water	EPA	Drinking water action level	0.015 mg/L
		WHO	Drinking water Quality Guidelines	0.01 mg/L
	Bottled Water	FDA	Legal limit	No data

ter in plant leaves through foliar transfer and accumulate in cells [7]. In this sense, the aerial parts of plants (leaves, flowers, seeds, and grains) and food products made from these parts can be useful indicators for monitoring the long-term risk of airborne heavy metal pollution.

Determination of nutrient and toxic elements in food samples can be carried out using inductively coupled plasma-optical emission spectrometry (ICP-OES) [8-11] inductively coupled plasma mass spectrometry (ICP-MS) [12-14], flame atomic absorption spectrometry (FAAS) [15-17], and graphite furnace atomic absorption spectrometry (GFAAS) [18-21]. Among the spectrometric techniques used for elementary determination, ICP techniques are outstanding due to their wide linear response, low limits of detection (LODs), multielementary capability, fast analysis, good precision, and accuracy [22].

In this context, this study aimed to determine certain essential and non-essential heavy metal constituents of wheat flour commercialized in Çorum, Turkey using inductively coupled plasma-optical emission spectrometry (ICP-OES). Çorum, the capital of the ancient Hittite civilization, is a province in the Black Sea Region of Turkey. Çorum is a good sampling point for monitoring heavy metal contamination in an agricultural crop because it is transforming its agriculture-based economy into industry, improving flour mills, tile and brick production, and offering performance in various industrial fields [23].

MATERIALS AND METHODS

Reagents and Apparatus

All chemicals were of analytical grade (Merck, Germany; Alfa Aesar, Germany; Sigma Aldrich, Germany) and

were used without further purification. All flour samples cultivated in Çorum were purchased from the local markets in Çorum, Turkey. Samples were prepared by the wet fractionation method. Before analysis, samples were diluted with distilled water (18.2 MΩ cm^{-1}), which was filtered (Whatman #42 filter paper) and then purified with a water purification system (MES MP Minipure, Turkey). All analytical weighing was performed using a Precisa/321LX-220A balance (Precisa Gravimetrics AG, Switzerland). The dry weight of the flour samples was recorded after drying in the oven (Nüve FN055 Ankara, Turkey) at 105 ± 5°C until a constant weight was obtained.

Sample Preparation and Heavy Metal Determination by ICP-OES

To avoid contamination, all glassware was soaked in nitric acid solution for more than 24 h and rinsed with deionized water before use.. The samples were dried in the oven at 105 °C until they reached a constant weight. The complete digestion of wheat flour samples was achieved according to the procedure described by Araujo et al. [24] and Shar et al. [25]. Briefly, the wheat flour samples were digested with concentrated nitric acid and hydrogen peroxide in glass vessels on a hot plate. Then, the contents of the glass vessels were cooled, transferred to volumetric flasks, and diluted with high-purity water. Three replicates of acid digestion were performed for each sample.

The quantitative analysis of all samples was carried out using an inductively coupled plasma optical emission spectrometer (ICP-OES) (ARCOS FHE12, SPECTRO, Germany). Plasma operating conditions and selected wavelengths were used as recommended by the manufacturer. ICAL solution (ICP-OES ICAL Solution for Spectro in 2% HNO_3 / 2% HCl 250 mL) was used for self-checking and self-adjustment of the instrument. The instrument conditions and parameters are given in Table 2.

Table 2. Operating conditions for ICP-OES analysis

Plasma Power (W)	1400
Gas flow (L/min)	
-Coolant	13.0
-Auxiliary	0.80
Nebulizer type	Crossflow
Nebulizer flow rate (L/min)	0.90
Pump speed (rpm)	30
Stabilization time (s)	0
Number of probes for each measuring	3
Plasma observation	Axial

The sample solutions were scanned using ICP-OES to determine the approximate element contents. After scanning, three elements (Cu, Zn, and Pb) were selected for quantification, and 7-point (including the method blank solution) calibration curves were performed for these elements. The appropriate calibration solutions were prepared by diluting 1000 mg L^{-1} mono elemental stock solutions. After the calibration, each replicate of acid digestion was analyzed three times with ICP-OES.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated as 3 and 10 times the standard deviation (σ) for 10 repetitive injections of the blank solution, respectively, divided by the slope of the calibration graph. To assess the accuracy of the method, spike and recovery experiments were carried out.

Statistical Analysis

The significance of the differences between the mean content of items obtained from different groups was determined by one-factor analysis of variance (ANOVA). AP ≤ 0.05 was considered a statistically significant level.

RESULTS AND DISCUSSION

The purpose of this study was to determine the heavy metal content of wheat flour samples from various brands (labeled as S1, S2, S3, S4, and S5) in order to evaluate their suitability as a bioindicator for monitoring long-term changes in environmental pollution in Çorum. As known that the elements such as sodium (Na), aluminium (Al), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), titanium (Ti) and manganese (Mn) are earth crust elements or soil tracers, on the other hand, vanadium (V), chromium (Cr), cadmium (Cd), nickel (Ni), copper (Cu), lead (Pb), zinc (Zn), arsenic (As), tin (Sn) and selenium (Se) can be considered partially natural in origin and partially anthropogenic depending on the source region and travel path of the air mass [26]. Of the monitored anthropogenic tracers by ICP-OES, Cu, Zn and Pb were detected in appreciable quantities in all flour brands, therefore, only these three heavy metals were monitored in subsequent studies.

Firstly, the accuracy of the proposed ICP-OES method was evaluated by spike and recovery studies. The method blank solution was spiked with Cu, Zn, and Pb ions at a concentration of 0.20 mg L^{-1}. The spiked sample and the method blank were analyzed with the given instrument parameters. Table 3 shows the detection wavelength of each element, the correlation coefficients (R^2), LOD, LOQ, and percent recovery. Good recovery values in the range of 99.5 to 101% indicate that the proposed method is accurate.

The same method was used for the determination of Cu, Zn, and Pb content in five flour samples supplied in 2016.

Table 3. Detection wavelength, the correlation coefficients, LOD, LOQ, and percent recovery for Cu (II), Zn (II), and Pb (II)

Element	Detection wavelength (nm)	Correlation coefficient (R^2)	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Recovery (%)
Cu (II)	327.396	0.99999	0.003	0.010	99.5
Zn (II)	213.856	0.99999	0.002	0.007	100.5
Pb (II)	220.353	0.99996	0.007	0.023	101.0

New 7-point calibration curves were constructed so that the middle of the calibration ranges represented the element concentrations of the sample. The concentrations of Cu, Zn, and Pb in the five flour sample digests determined using ICP-OES are presented in Table 4.

Table 4. Average concentrations and standard deviations of Cu, Zn, and Pb obtained for wheat flour samples by ICP-OES (dry weight basis) (in 2016)

Sample	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
S1	2.155±0.111	11.374±1.102	2.009±0.562
S2	2.488±0.128	9.831±1.361	1.617±0.574
S3	2.897±0.155	13.467±1.457	1.574±0.582
S4	3.073±0.164	13.599±1.172	2.201±0.672
S5	3.182±0.203	14.706±1.824	1.915±0.772

In our study, Zn (II) and Cu (II) concentrations ranged from 9.8 to 14. 7 and 2.2 to 3.2 mg kg^{-1} for different brands of flours, respectively. These elements are essential micronutrients for plant growth, development as well as human health. According to the FDA [27], a daily Cu intake of 2 mg a Zn intake of 15 mg for adults is recommended. In this study, while As (III), Cd (II), and Hg (II) were below the detection limit of the instrument, the amount of Pb (II) in flour samples varied from 1.5 to 2.2 mg kg^{-1}. According to guidelines set by The European Commission [28], Pb concentrations have exceeded the maximum permissible concentration (0.2 mg/kg). Summary ANOVA statistics of Cu (II), Zn (II), and Pb (II) concentrations in the flour samples studied are shown in Table 5.

The ANOVA results suggested that the Cu and Zn contents of S1 and S2 were significantly different from each other and the other samples ($P \leq 0.05$). However, there was no significant difference in Cu (II) ($P = 0.137$) and Zn (II) ($P = 0.108$) concentrations between S3, S4, and S5. The one-way ANOVA did not find a significant difference among the sample groups concerning the concentration of Pb (II) ($P = 0.374$). According to these results, flour samples labeled S3, S4, and S5 did not show statistically significant differences in terms of Cu (II) ($P = 0.137$), Zn (II) ($P = 0.108$), and Pb (II) ($P = 0.267$) concentrations. The ANOVA test, however, revealed statistically significant differences in the Cu and Zn distributions of the S1 and S2 samples when compared to the other samples ($P \leq 0.05$). The heavy metal uptake patterns can provide insight into the differences in metal accumulation between the samples examined in this study. The discussion that follows is divided between these two; with Cu and Zn defined as micronutrients and with Pb considered a toxic and non-essential heavy metal for plant growth.

Table 5. One-way ANOVA results of Cu (II), Zn (II), and Pb (II) concentrations for all sample groups

Source	Cu (II)	Zn (II)	Pb (II)
S1-S2	≤ 0.05	≤ 0.05	0.257
S2-S3	≤ 0.05	≤ 0.05	0.899
S3-S4	0.201	0.892	0.095
S4-S5	0.450	0.089	0.478
S1-S3	≤ 0.05	≤ 0.05	0.214
S1-S4	≤ 0.05	≤ 0.05	0.592
S1-S5	≤ 0.05	≤ 0.05	0.807
S2-S4	≤ 0.05	≤ 0.05	0.115
S2-S5	≤ 0.05	≤ 0.05	0.441
S3-S5	0.056	0.085	0.383
S3-S4-S5	0.137	0.108	0.267
S1-S3-S4-S5	≤ 0.05	≤ 0.05	0.393
S2-S3-S4-S5	≤ 0.05	≤ 0.05	0.299
S1-S2-S3-S4-S5	≤ 0.05	≤ 0.05	0.374

$P < 0.05$ was assumed as a statistically significant level.

Soil is a major source of nutrients needed by plants for growth and development. Since Çorum province is known for copper, lead, and zinc mining, therefore, soil can be considered to be the major source of Cu, Zn, and Pb found in the flour samples. It is known that the transfer of essential (micronutrients) and non-essential heavy metals from the soil to cultivated plants depends on soil properties and therefore may differ widely among areas [29]. Thus, the lack of statistically significant differences between S3, S4, and S5 flour samples in terms of Cu (II), Zn (II), and Pb (II) contents may be explained by the fact that these flour samples might be produced from wheat grains cultivated on similar agricultural soil. On the other hand, the significant differences in Cu and Zn contents of S1 and S2 samples compared to each other and other samples may be due to the different chemical and physical properties of the agricultural soils where the wheat is grown. However, no significant difference in Pb (II) concentration between all samples indicates that Pb has not mainly originated from agricultural sources. In our study, as mentioned above, the Pb contents of wheat flours exceeded the maximum permissible concentration (0.2 mg/kg). A more probable scenario for the high levels of Pb obtained for all samples can be air pollution.

The main heavy metals entering the roots of plants

from the soil are transported to the aerial parts via the xylem and phloem [30]. Accordingly, Cu and Zn can be transported from the roots to the grains as they are essential micronutrients for wheat. On the other hand, Pb, which has no known function in plant metabolism, is likely to pass from soil to plants. However, cellular mechanisms exist in their structures to control the transfer of toxic heavy metals that are likely to pass through the soil to the aerial parts of plants. It has been reported in the literature that Pb transfers and accumulates to the parts above the soil and into the grains of the plants. It was observed that the specified lead amounts were less than the basic element amounts [31, 32]. It has also been stated that approximately 5% of Pb is transferred to airborne components and 95% accumulates in the roots [33, 34]. Guo et al. investigated the accumulation of Pb, As and Cd in their study on 16 wheat species and found that their concentrations decreased significantly in the root, leaf, and stem parts of wheat, respectively [35]. Accordingly, it was concluded that the roots acted as a barrier to prevent Pb transfer to various parts of the wheat, and thus the edible parts of the plant were protected from harmful lead amounts [31, 35]. Pb isotopes were used in the investigation of the main Pb sources in the wheat grain and it was reported that the effective factor causing the increase in Pb concentration was not soil [36]. In the light of these findings, it was decided to analyze the seasonal flour samples of the same brands after two years and compare the results with the air pollution data.

In 2018, seasonal flour samples with the same brand (S1 and S2) were purchased from the local markets and analyzed with the same method and instrument (S3, S4, and S5 brands could not be supplied as their production was discontinued). Table 6 shows the average concentrations of Cu, Zn, and Pb obtained for wheat flour samples collected in 2018.

Table 6. One-way ANOVA results of Cu (II), Zn (II), and Pb (II) concentrations for all sample groups

Sample	Cu (II) (mg/kg)	Zn (II) (mg/kg)	Pb (II) (mg/kg)
S1	2.162±0.022	10.354±1.162	2.956±0.521
S2	2.493±0.181	9.646±1.064	2.861±0.426

The results from ANOVA indicated that there was no significant difference between S1-2016 and S1-2018 in terms of Cu (II) (P = 0.993), and Zn (II) (P = 0.084) contents. In addition, one-way ANOVA found also no statistically significant difference in Cu (II) (P = 0.948), and Zn (II) (P = 0.784) concentrations between S2-2016 and S2-2018. However, the mean concentrations of Pb (II) in the S1-2018 and S2-2018 samples were significantly higher in comparison to those in the S1-2016 and S2-2016 samples, respectively ($P \leq 0.05$). According to this, the Pb (II) content of the S1 and S2 samples increased by approximately 47% and 77%, respectively, over a two-year period. This increase can be mainly associated with air pollution This increase can be mainly associated with air pollution. To test this hypothesis, the annual average change in air quality was examined.

The flour samples purchased for this study were produced from winter wheat, the main crop cultivated in Çorum, whose sowing and growing period is from October to July of the following year. Since planting, growing and harvesting of wheat takes approximately nine months, the air pollution data from 2015-October to 2016-July (this period was abbreviated here as P1) and from 2017-October to 2018-July (this period was abbreviated here as P2) were taken into account to interpret the increase found in the Pb contents of the samples. Air quality data used in this study were collected at two stations (Bahabey - 40.55° N, 34.96° E, and Mimar Sinan - 40.53° N, 34.94° E) in Çorum. Today, pollutants such as SO_2, PM_{10}, $PM_{2.5}$, NO_x, NO_2, NO, CO, and O_3 are continuously measured at these stations. In P1 and P2, however, only four of the pollutants (PM_{10}, NO_X, NO_2, and CO) in Bahabey (B) station and two of them (PM_{10}, SO_2) in Mimar Sinan (MS) station were monitored.

Fig. 1 shows the change in the number of different pollutants obtained from the two stations between P1 and P2 (measurements on the same day at both stations were taken into consideration, and the means of each data was normalized for easy comparison)

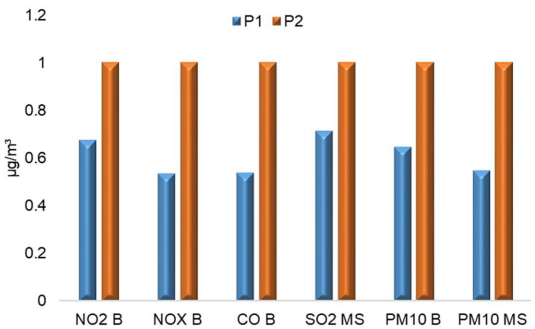

Figure 1. The concentration changes of various pollutants at Bahabey (B) and Mimar Sinan (MS) stations between P1 (2015-October to 2016-July) and P2 (2017-October to 2018-July) (data were normalized)

As can be seen from Fig. 1, NO_2, NO_X, and CO concentrations increased by 48% ($P \leq 0.05$), 87% ($P \leq 0.05$), 86% ($P \leq 0.05$), and 40% ($P \leq 0.05$), respectively, after 2 years. However, a one-way ANOVA found no statistically significant difference in SO_2 concentration (P = 0.143) between the P1 and P2 periods. The greatest sources of these pollutants in the atmosphere are the burning of fossil fuels and the emissions from vehicles as well as industrial sources [37, 38]. According to data obtained from B and MS stations, PM_{10} levels increased by 82% ($P \leq 0.05$), and 55% ($P \leq 0.05$), respectively, in the same period. Primary sources of PM_{10} are incomplete combustion, automobile emissions, and dust. In addition, nitrogen dioxides are the precursor of harmful secondary

air pollutants such as ozone and particulate matter [37, 39, 40]. It can be suggested that observed increases in air pollution are a result of rapid industrialization and increased traffic activities and coincide with the increment in Pb levels found for S1 (47%) and S2 (77%). Therefore, it can be said that the wheat grains used for the production of S1 and S2 flour samples may have been grown in the air-polluted area. Similar results were reported in the literature. Zhao et al. reported the Pb concentrations in wheat grain samples collected in the 1982 and 1998 and indicate that, in 1998, 13 years after the enforced reduction of Pb added to petrol, there was a clear shift toward lower Pb concentrations in wheat grain [41]. Ma et al. showed that 206Pb/207Pb ratios in wheat grains at the high- and low-deposition areas were close to that of atmospheric deposition, indicating that Pb in the wheat grains was largely derived from atmospheric deposition [42]. Ma et al. indicate that Pb concentration and bioavailability in the atmospheric deposition samples were markedly higher than those in the soil, facilitating easier Pb absorption by plants [43]. Therefore, Pb pollution in the atmosphere might be the main source of Pb contamination for wheat in the study area, similar to the case for most farmlands in the main grain wheat-producing areas in the North China Plain.

The findings of this study have to be seen in the light of some limitations. The primary limitation to generalizing these results is the lack of a sufficient number of specimens. Although all five flour brands, produced from wheat grown in Çorum, were supplied at the beginning of the study, two years later only two flour samples could be collected from local markets, as the production of the other three brands was discontinued. The second limitation is related to the lack of information about the water quality, soil quality, plant physiology, heavy metal concentration in atmospheric PM, and exposure conditions. However, several studies, as mentioned before, have revealed that fallout from atmospheric PM can be the main source of heavy metal pollution in plants by foliar transfer; especially for lead, which has relatively low mobility in soil and is generally weakly photo available by root uptake [44]. Therefore, despite the limitations, we think that the hypothesis that Pb contamination in flour samples is mainly caused by atmospheric pollution has been supported by the data presented in this study. Nevertheless, further studies are necessary to monitor the long-term effect of air pollution on other food products and human health.

CONCLUSION

The investigation in the fast-industrializing city, Çorum, indicated that Pb concentration (2.009, 1.617, 1.574, 2.201, and 1.915 mg/kg) in wheat flour samples grown and produced in this region was higher than the corresponding guideline values (0.2 mg/kg). The statistical discrepancies ($P \leq 0.05$) and similarities ($P > 0.05$) in the concentrations of Cu and Zn in these samples could be attributed to different or similar cultivation lands. On the other hand, no significant difference ($P = 0.374$) in Pb concentration between the all samples indicates that the source of the Pb contamination may be air pollution. In this context, the increments of Pb content obtained for seasonal flour samples of the same brands after two years were statistically compared with air quality data, and found a correlation between them. According to data obtained from Bahabey and Mimar Sinan stations, the PM_{10} level increased by 82%, and 55%, respectively, which coincides with the increments in Pb levels found for sample 1 (47%) and sample 2 (77%). Finally, it has not been possible to examine all the factors that may cause the increase, but it has been demonstrated that the increase in Pb content in flour samples is consistent with the increase in air pollution parameters, and the rapid industrialization in Çorum may be one of the important factors causing heavy metal pollution in the final product.

CONFLICT OF INTEREST

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manyscript.

AUTHOR CONTRIBUTION

The creation of ideas and hypotheses for the research, the planning of the methods to obtain the results, and the follow-up of the organization of the study were carried out by E Gokmese, E Olmez, U Ergun and F Gokmese. Data collection, arrangement and reporting were made by E Olmez. E Olmez and U Ergun did an analysis and interpretation of the data. The writing of the article was undertaken by E Gokmese and E Olmez. Before the article was sent, the final review in terms of grammar and content was made by F Gokmese and U Ergun.

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