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Heavy Metal Pollution in Olives Grown in Bursa, Turkey

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Heavy metal pollution is one of the most important environmental problems. The toxic effects of metals and their accumulation throughout the food chain lead to serious ecological and health problems. In this study, the accumulation of lead, cadmium, iron, copper and zinc in olives (*Olea europaea*) collected from a field situated near busy roads and industrial areas was investigated. Samples were collected at distance of 5-20 m from the road. Olive samples were obtained from 90 orchards in Mudanya, Gemlik and Orhangazi (Bursa, Turkey). Atomic absorption spectrophotometer (AAS) was used to determine these metals. The mean of Pb, Cd, Fe, Cu and Zn levels were found in the studied samples were 1362.23 ± 4.94 µg/kg-wet weight(ww), 158.29 ± 1.12 µg/kg-ww, 66.37 ± 2.03 mg/kg-ww, 6.51 ± 0.79 mg/kg-ww and 5.76 ± 0.79 mg/ kg-ww, respectively.

Key Words: *Olea europaea*, AAS, Heavy metals, Accumulation.

INTRODUCTION

In recent years particular scientific interest has been focused on Mediterranean diet. This term refers generically to the largely plant-based dietary pattern of countries surrounding or being surrounded by the Mediterranean sea[1,2]. In general, Mediterranean diet is characterized by a high intake of fruits, vegetables, cereals, beans, nuts, poultry, fish, dairy products with less red meat. Olive oil is the principle source of fat in Mediterranean diet. Several studies have suggested that the Mediterranean diet is associated with lower incidence of cardiovascular disease and prostate and colon cancer[3-7].

Table olives and olive oil are traditional Mediterranean foods. From olive growing, processing to the finished product, science and technology can continue to develop the competitive quality of olive products. The olive agri-food chain could capitalize on these potentially, numerous opportunities in the new Millennium or instead, may fail to invest in scientific creativity and innovation to benefit olive product quality[8].

Heavy metals pollution is a major environmental problem in the world. Heavy metals can be harmful for plants, humans and animals. Heavy metal residues of smelter, fuel, coal, car exhaust, pesticides, fertilizers and mine contaminate olives.

If the agricultural areas are close to residential areas, alongside motor roads and industrial areas, agricultural products are more affected by heavy metals.

Consequently, the aim of this study has been to determine the contents of lead, cadmium, iron, copper and zinc in post harvest olive grown up alongside motor roads and industrial areas.

EXPERIMENTAL

Location of the research: The province of Bursa, located in the northwestern part of Turkey, is the fourth biggest city and industrial center of Turkey. It is a rapidly growing city and its present population is estimated to be over 2,106,000.

Bursa has been gradually developing into an important industrial city in Turkey. Textile industry (11), automotive production plants (9), machinery industry (10), metal industry (10), chemical industry (4), wire-cable industry (2) and fertilizer industry (1) are the main industrial activities in these districts. These industries are creating heavy pollution problems such as Pb, Cd and Cu. Bursa has a heavy traffic problem due to its own traffic but also because it is located on the route to other important cities in Turkey such as Istanbul, Izmir and Ankara. Traffic and industrial activities are the main sources of the metal pollutants.

Samples and sampling zone: Black olive samples from 'Gemlik' variety were collected from beginning of September to February in 2002-2003. Three different areas (Mudanya, Gemlik and Orhangazi) chosen from the most contaminated parts of the city of Bursa represented the sampling sites. Olive is an important commercial product in these regions. Fruits samples were collected from 90 areas when fully ripe. At each sampling station, sufficient amounts of olive samples were hand-picked from all sides of trees which grew up 5-20 m far from the motor road. The traffic density of the road was estimated to be 31,080 vehicles/day[9]. Samples from the industrial areas were taken from different places between 50 and 100 m around the factories. The collected samples for each field were placed in polyethylene bags and then olive seeds were removed by hand, flesh was homogenized, put into polyethylene containers and stored in a deep-freezer at -20 ºC until usage. As a control, olives grown in uncontaminated area were analyzed.

Methods: The digestion processes necessary to eliminate organic compounds and transfer the inorganic elements to the soluble phase were accomplished using a Fostecator 2012 digester system and its accessories[10]. For digestion of the samples, a combination of nitric acid (65 %; Merck, UK) and hydrogen peroxide (35 %; Merck, UK) was used. After digestion, the samples were diluted and kept at 8 ºC in polyethylene containers until analyzed[10,11].

An atomic absorption spectrometer (Shimadzu AA-6701) equipped with deuterium background correction and a GFA-6500 graphite furnace atomizer were used for AAS measurements. The graphite furnace absorption spectrometry method was used for the determination of the lead and cadmium levels, while the flame atomic absorption spectrometry method was used for measuring the levels of iron, copper and zinc in the digested samples[12]. Measurements were made using the hollow cathode lamps for all of the metals. The main instrumental parameters are summarized in Table-1.

TABLE-1
INSTRUMENTAL CONDITIONS FOR AAS DETERMINATION OF THE STUDIED METALS

Metal	Wavelengths (nm)	Slit widths (nm)	Lamp current (mA)
Pb	283.3	0.5	10
Cd	228.8	0.5	8
Fe	248.3	0.5	12
Cu	324.8	0.5	6
Zn	213.9	0.5	8

An air-acetylene flame was used for the flame AAS measurements. Pyrolytically coated graphite cuvettes and argon gas were used in electrothermal AAS measurements. The graphite furnace operating conditions for Pb and Cd are given in Table-2. The elimination of interference effects of the matrix on Pb and Cd determinations was necessary. A palladium salt (High-purity standards MM-9100) has been suggested as the matrix modifier[13,14].

TABLE-2
GRAPHITE FURNACE OPERATING CONDITIONS

Step	Lead			Cadmium		
	Temperature (ºC)	Time (s)	Flow rate (L min^{-1})	Temperature (ºC)	Time (s)	Flow rate (L min^{-1})
1	120	20	1.00	120	20	1.00
2	250	10	1.00	250	10	1.00
3	300	10	1.00	300	10	1.00
4	300	3	0.00	300	3	0.00
5	1800	3	0.00	1500	3	0.00
6	2200	6	1.00	2000	6	1.00

The quantification of the studied metals was performed by the standard addition method, which minimizes the interference effects. The results of the recovery test are shown in Table-3. Six replicate readings were taken for each sample and mean values of these figures were used to calculate the concentrations.

TABLE-3
RESULTS OF THE RECOVERY TEST

Metals	Added (mg L^{-1})	Found (mg L^{-1})*	Recovery (%)
Pb	5.00	5.00 ± 0.15	100.1
Cd	5.00	5.03 ± 0.11	100.6
Fe	5.00	5.02 ± 0.08	100.4
Cu	5.00	4.95 ± 0.10	98.9
Zn	5.00	4.99 ± 0.12	99.8

*Mean ± SD (n = 6).

Statistical analysis: The one-way analysis of variance was applied for the statistical evaluation of the obtained results. It was designed by using the pocket program of the Minitab 12.0 software (Minitab Inc., State Collage, PA, USA). LSD ($p < 0.05$).

RESULTS AND DISCUSSION

The concentrations of metals found in the studied samples are given in Table-1. Lead is especially toxic to humans, animals and plants for this reason its concentration has been limited in food by different standards[15-17]. Table-4 showed the lead values of post harvest olive samples vary between 778.11 and 3680.90 µg/kg-wet weight. The samples with higher Pb concentration are from Gemlik and Orhangazi, since these areas are characterized by high traffic load and industrial emission. These levels of lead don't cause toxic symptoms, but they are high according to the Codex standards for table olive. In several reports, it is normally observed that the content of some metals including Cd and Pb in the different plant species decrease with increasing distance from the road[18-21]. This is mainly due to the complexity of the absorption of a metal pollutant by plant from the atmosphere and the soil and the presence of numerous variables[20]. Rovinsky *et al.*[22] observed that in the background areas of the European countries the ratio between the highest and the lowest content of Pb was 5, whereas the mean concentrations of lead in the plant leaves varying in the range of 1-5.5 mg/kg.

Agricultural uses of phosphate fertilizers and sewage sludge and industrial uses of cadmium have been identified as a major cause of widespread dispersion of the metal at trace levels into the general environment and human foodstuffs[23]. Cadmium induces serious peroxidation in membrane structures. Due to these negative effects, it has been associated with several diseases. In addition, cadmium is weakly mutagenic and has been shown to have carcinogenic activity[24]. The content of the Cd in the studied olives varied from 61.47-356.44 µg/kg-wet weight. Samples from Orhangazi area presented the highest levels of Cd. According to Oliva and Valdes[25], the highest content of cadmium found in plants grown in polluted areas was determined in roots, leaves and fruits.

Iron is also an essential metal in plants and constituent of many enzyme systems that have an important function in the oxidation-reduction processes. The levels of Fe detected in olive Mudanya, Gemlik and Orhangazi regions vary between 14.36, 47.12 and 118.55 mg/kg-ww, respectively. The samples with higher Fe concentration came from Orhangazi and Gemlik, being close to motor roads and industrial areas. These pollution factors increase soil acidity. Acid conditions enhance the mobility of iron when the pH value of soil is less than 4.0 and the leaching rate is about double of that in neutral conditions[26]. Caselles *et al.*[27] reported that the high levels of Fe detected in petunia leaves in urban areas after 9 weeks compare with those in suburban areas may indicate that Fe is absorbed both by the leaf cuticle and by the roots and Fe concentration in the leaves of petunia plants grown in urban areas is very high.

TABLE-4
METAL CONTENTS OF POST HARVEST OLIVE SAMPLES

Metals	Provinces	Sample counted	Mean ± SD	Range
Lead (µg/kg-ww)	Mudanya	30	861.18 ± 3.98	589.42-1376.23
	Gemlik	30	1610.63 ± 6.08	857.18-3695.21
	Orhangazi	30	1608.14 ± 4.67	778.11-2657.48
	Control	–	425.51 ± 2.86	–
	Total	90	1362.23 ± 4.94	589.42-3695.21
Cadmium (µg/ kg-ww)	Mudanya	30	112.43 ± 0.92	59.34-275.28
	Gemlik	30	151.07 ± 0.87	65.78-369.14
	Orhangazi	30	182.98 ± 0.71	70.08-348.75
	Control	–	45.56 ± 0.22	–
	Total	90	158.29 ± 1.12	59.34-369.14
Iron (mg/kg-ww)	Mudanya	30	22.11 ± 2.03	6.85-51.33
	Gemlik	30	56.72 ± 1.97	9.63-129.38
	Orhangazi	30	102.14 ± 2.11	10.05-146.32
	Control	–	5.97 ± 0.34	–
	Total	90	66.37 ± 2.03	6.85-146.32
Copper (mg/kg-ww)	Mudanya	30	4.76 ± 0.43	2.85-7.64
	Gemlik	30	7.14 ± 0.85	3.78-10.22
	Orhangazi	30	6.98 ± 0.54	3.41-13.01
	Control	–	2.10 ± 0.38	–
	Total	90	6.51 ± 0.79	2.85-13.01
Zinc (mg/kg-ww)	Mudanya	30	5.44± 0.82	3.64-9.02
	Gemlik	30	5.69 ± 1.11	3.79-11.53
	Orhangazi	30	6.78 ± 0.47	2.19-10.25
	Control	–	2.18 ± 0.09	–
	Total	90	5.76 ± 0.79	2.19-11.53

The behaviour of the copper studied does not suggest a regular gradient as the distance from the motor road and industrial area increases[20], but this metal affected by using the metal-based fungicides and pesticides[28,29].The origin of Zn in olives samples are derive mainly from abrasion of tyres and brake disks[30]. Copper and zinc are essential elements in all high plants and play important functions in several physiological processes like, photosynthesis, respiration, protein metabolism and are important constituents of many enzymes[31]. However high doses of these metals in food, they occur negative effects on human health. Present results indicate that the accumulation value for Cu and Zn in olives were 2.85-13.01 mg/kg-ww, 2.19-11.53 mg/kg-ww, respectively. Dmuchowski and Bytnerowski[32], found Cu and Zn concentration in plant ranging from 2-20 mg/kg and 10-100 mg/kg, respectively. Öztürk and Türkan[33] observed a mean content of zinc of 40 mg/kg in *Olea europaea* grown 2 m far from the road.

In some soil samples of Bursa plain, the values of Fe ranged from 29.7 to 62.5 g kg^{-1}, Zn from 0.060 to 0.407 g kg^{-1} and Cu from 0.056 to 0.165 g kg^{-1}. Cadmium varied[34] from 0.0015 to 0.0063 g kg^{-1} and Pb from 0.017 to 0.052 g kg^{-1}.

Trace elements in the atmosphere of Bursa were collected and analyzed for Cu, Zn, Pb, Cd and Fe elements. The concentration was obtained for Fe (2165.4 ± 1717.4 ng/m^3), Cu (396.7 ± 391.7 ng/m^3), Zn (250.5 ± 178.5 ng/m^3) and Cd (0.7 ± 0.9 ng/m^3). The elevated concentrations of Cu, Zn and Pb can be attributed to the industrial activities and heavy traffic near the sampling site[35,36].

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