International Journal of Farming and Allied Sciences
Available online at www.ijfas.com
©2012 IJFAS Journal-2012-1-3/77-81
ISSN 0000-0000 ©2012 IJFAS

Monitoring of heavy metal and minerals in different parts of oak acorn (*Quercus* spp.)

Mehmet Musa Özcan[1*], Coşkun Sağlam[2] and Mustafa Harmankaya[3]

1- Department of Food Engineering, Faculty of Agriculture, University of Selçuk, 42031 Konya, Turkey
2- Selcuk University, Cumra High Educational College, 42500 Çumra- Konya/ Turkey
3- Department of Soil Science, Faculty of Agriculture, University of Selçuk, 42031 Konya, Turkey

Corresponding author Email: *mozcan@selcuk.edu.tr*

ABSTRACT: The mean crude protein and ash, heavy metal and minerals of acorn fruit and hulls were determined by ICP-AES. The mean values of Al, B, Cr, Cu, Fe, Mn, Ni and Zn contents of fruit hulls varied from 6.4 to 42.9, 5.8 to 10.2, 0.0 to 0.2,5.3 to 13.8, 13.7 to 65.1,1.7 to 9.6, 0.0 to 0.2 and 2.5 to 16.0 (mg/Kg, dw), respectively. In addition, Al, B, Cr, Cu, Fe, Mn, Ni and Zn values of acorn fruits were found at the levels between 0.5 to 10.8, 5.4 to 10.0, 0.034 to 0.136, 5.5 to 10.4, 17.5 to 392, 10.3 to 43.1, 0.000 to 0.295 and 3.3 to 17.9 (mg/Kg, dw), rspectively. In regard to macro elements of fruit and corresponding hulls, the mean values of Ca, K, Mg and P of hulls were found between 1632 to 4222, 1447 to 7762, 236 to 752 and 848 to 1274 mg/Kg (dw), respectively. K levels of samples was found at the highest concentrations.

***Keywords*:** oak, acorn fruit, hulls, , heavy metal,minerals, ICP-AES

INTRODUCTION

Oak accorns have been under exploitation for livestock feeding (Bouderoua ad Selselet-Attou, 2003), as an energy source (47-60% starch) (Kekos and Kaukios, 1985) and for oil extraction (7-14.4% lipids) (Ofcarcik and Burns, 1971). Oak uses include almost anything that mankind has ever derived from trees such as timber, food for man, feed for animals, tannins and extractives. Oak acorns are of mjaor importance to man and animals (Cordain et al. 2000). Al-Jassim et al. (1998) have also used concentrate diets containing oak acorns and urea to feed Awassi lambs in Jordan. Oak acorns may serve as a good and cheap source of energy and minerals. Also, oak accorns were used as food either directly or as a supplement ingredient of products such as bread (Jacknis, 2004). Although heavy metals are natural comonents of the environment, they are emitted into the environment in different ways; through natural sources suc as continental dust, volcanic dust and gas, sea spray and biogenic particles industry, agriculture and other anthropagenic activities (Başlar et al. 2009; Aksoy et al. 2000). Human activities have globally affected the biogeochemical cycling of heavy metals, resulting in a progressive increase in the flux of bioavailable chemical forms to the atmosphere (Ng et al. 2005; Yorek et al. 2008; Yıldız et al. 2010). Biomonitoring provides the cheapest and simplest method for monitoring trace metal elements inthe atmosphere (Kaya and Yama, 2008; Cayır et al. 2008; Başlar et al. 2009; Yıldız et al. 2010).
The aim of this study was to present and investigate the concentrations of protein, ash, heavy metal, micro- and macro elements in oak fruit and corresponding hulls.

MATERIAL AND METHODS

Plant materials

Acorn fruits were collected from naturally grown in Isparta and Konya in Turkey, *Quercus vulcanica , Quercus cerris var. cerris , Quercus trojana , Quercus coccifera , Quercus pubescen* , *Quercus ithaburensis* subsp. *macrolepis, Quercus robur subsp. robur and Quercus libani,* during the maturation season starting between October and November 2010. A composite sample of three kg of ripe oak acorns (including cupules), for each species were collected from site representing the major geographical distribution of oak in Isparta and Konya Provinces. The herbarium materials were identified by Dr Coşkun. Herbarium numbers 301,302,303,304,305,306,307 and 308 for *Quercus vulcanica* , *Quercus cerris* var. *cerris* , *Quercus trojana* , *Quercus coccifera* , *Quercus pubescens* , *Quercus ithaburensis* subsp. *macrolepis, Quercus robur* subsp. *robur and Quercus libani*, respectively. Acorn fruit and hulls were individually ground, and dried at 70 ^{o}C for 24 h. Each one material was analysed separately for mineral and heavy metals.

Reagents

All reagents used in experiment were of analytical reagent grade. Double deionized water was used for all solutions. In addition, sulphuric acid, nitric acid and hydrogene peroxide were of supra-pure quality (Merck-Darmstadt). Also, all the plastic and glass materials were cleaned by soaking in dilute H_2SO_4, and were rinsed with distilled water prior to use.

Determination of mineral contents

Collected samples were dried at 70 ºC in a drying cabinet with air-circulation until they reached constant weight. Later, about 0.5 g dried and ground sample was digested by using 5ml of 65% HNO_3 and 2 ml of 35% H_2O_2 in a closed microwave system (Cem-MARS Xpress). The volumes of the digested samples were completed to 20 ml with ultra-deionized water and mineral concentrations were determined by inductively coupled plasma-optical emission spectroscopy (ICP AES; (Varian-Vista, Australia). Measurements of mineral concentrations were checked using the certified values of the related minerals in the reference samples received from the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) (Skujins,1998).

Working conditions of ICP-AES

Instrument :ICP-AES (Varian-Vista
RF Power : 0.7-1.5 kw (1.2-1.3 kw for Axial)
Plasma gas flow rate (Ar) : 10.5-15 L/min. (radial) 15 “ (axial)
Auzilary gas flow rate (Ar) :1.5 “
Viewing height : 5-12 mm
Copy and reading time :1-5 s (max.60 s)
Copy time : 3 s (max. 100 s)

Statistical analyses

Results of the research were analysed for statistical significance by analysis of variance (Püskülcü and İkiz.1989).

RESULTS AND DISCUSSION

The heavy metal and mineral contents of acorn obtained from each sampling site are given in Table 1, 2, 3 and 4. In addition, crude protein and ash contents of different layers of acorn were presented in Table 5 and 6, respectively. Present study was conducted to determine the current level of atmospheric heavy metal pollution in mountains (1070 m to 1608 m) of Isparta and Konya provinces. Eight different plants were collected to study their potential as biomonitors of heavy metal and micro elements (mg/Kg,dw).

The levels of heavy metal and micro elements were established by ICP-AES. The mean concentrationsof Al, B, Cr, Cu, Fe, Mn, Ni and Zn contents of fruit hulls of aorn varied from 6.4 to 42.9, 5.8 to 10.2, 0.0 to 0.2,5.3 to 13.8, 13.7 to 65.1,1.7 to 9.6, 0.0 to 0.2 and 2.5 to 16.0 (mg/Kg, dw), rspectively. In addition, Al, B, Cr, Cu, Fe, Mn, Ni and Zn values of acorn fruits were found at the levels between 0.5 to 10.8, 5.4 to 10.0, 0.034 to 0.136, 5.5 to 10.4, 17.5 to 392, 10.3 to 43.1, 0.000 to 0.295 and 3.3 to 17.9 (mg/Kg, dw), rspectively. While mean Al and Fe contents of acorn hulls were found at the hig levels, Fe and Mn were found high n acorn fruits. The highest Al (36.8 mg/Kg) and Fe (65.1 mg/Kg) in hulls were established in *Quercus vulcania*. In regard to macro elements of fruit and corresponding hulls, the mean values of Ca, K, Mg and P of hulls were found between 1632 to 4222, 1447 to 7762, 236 to 752 and 848 to 1274 mg/Kg (dw), respectively. K levels of samples **were** found at the highest concentrations. Phosphorus (9723 mg/Kg) was estabished as the highest element in hulls. Ca and P contents of hulls were determined higher than those of fruits.

Rababah et al. (2008) reported that acorn of Quercus species contained 141.17 and 278.17 mg/100 g Na, 75.98 and 148.81 mg/100 g K, 21.40 and 80.80 mg/100 P, respectively. The composition of acorn parts showed significant differences between the two parts in protein, ash, heavy metal and macro elements. Of the monitored trace elements in *Quercus cerris* L. Growing the Mt Bozdağ (1600 m) the highest concentration found was of Ni (0.080 µg/g,dw) followed by Zn (0.64), Fe (1.100), Pb (0.36) and Mn (0.525) (Yıldız et al. 010). By looking at the chemical composition of *Quercus* spp., one can recognise its potential as an agriultural product and its use as suplement in animal feed particularly in regions with a lack of animal feed due to local climatic conditions (Tanguy et al. 1977; Griffiths and Jones, 1977; Rao and Doesthale, 1982). Özcan and Bayçu (2005) reported that distributioal margin of the K levels were found between 7849 and15935 (µ/g,dw). Fe concentrations in the acorns of *Q.infectoria* subsp.*boissieri* (20711 µ/g), *Q.petraea* subsp petraea (2020.1 µ/g) and *Q.robur* subsp. *robur* (1453.7 µ/g)were in considerable amounts. The highest level of Zn concentration was detected in *Q.infectoria* subsp. *boissieri* (367.5 µ/g), while the lowest value was observed in Q.hartwissiana 16.9 µ/g). The lowest level of Cu was observed in *Q.infectoria* subsp *infectoria* (9 µ/g) (Özcan and Bayçu, 2005).

In our investigation, wide range of Fe concentratins between 13.7 to 65.1 and 17.5 to 39.2 mg/Kg for ulls and fruits, respectively, were determined. The highest values especially in Q.infectoria subsp boissieri (2071 µ/g), *Q.petreae* subsp. petreae (2020 µ/g) and *Q.robur* subsp. *robur* (1453 µ/g) implying the potential of Fe accumulation can be compared wih the grasses containing Fe within the range of 2127 to 3850 µ/g growing in soils derived from serpentine (Jhonston and Proctor, 1977).

Crude protein and ash contents of hulls of acorn fruits ranged from 7 g to12.0% (Table 5). The highest protein content was found in *Quercus robur* ssp. *robur*. Ash contents of the same varied from 1.1 (*Quercus vulcania*) to 2.0 % (*Quercus ithaburensis*). Crude protein and ash contents of acorn fuits were determined between 10.9 (*Quercus robur*) and 15.6% (*Quercus libani*), 1.1.% (*Quercus libani*) to 2.7% (*Quercus cerris*), respectively. As a result, both protein and ash contents of fruits were found at the high levels in comparison to hulls.

Largest variations of Al, Fe and Zn concentrations in *Quercus* and extremely different values in subspecies and variety levels were found. Significantly different concentrations of heavy metal and macroelements can be due to the constant genetical tolerance of acumulation, plant species, genetical difference, changing conditions of soil and climate.

Table 1. Heavy metal and micro element concentrations of acorn hulls of oak (mg kg^{-1}; dw; Data are presented as means ± SD, n = 3 replicates)

Samples	Al	B	Cr	Cu
Quercus vulcania	36.8 ± 1.9	10.2 ± 0.2	0.110 ± 0.011	9.2 ± 0.4
Quercus cerris var. cerris	16.3 ± 0.8	7.2 ± 0.1	0.074 ± 0.007	8.9 ± 0.3
Quercus trojana	6.4 ± 0.9	7.4 ± 0.3	0.040 ± 0.007	8.4 ± 0.3
Quercus coccifera	13.0 ± 1.4	5.8 ± 0.1	0.064 ± 0.001	13.8 ± 1.2
Quercus pubescens	13.3 ± 1.8	7.9 ± 0.2	0.150 ± 0.009	8.9 ± 0.3
Quercus ithaburensis ssp. macrolepis	35.2 ± 1.1	8.2 ± 0.2	0.110 ± 0.011	5.2 ± 0.1
Quercus robur ssp. robur	21.8 ± 2.4	9.6 ± 0.8	0.131 ± 0.006	5.6 ± 0.5
Quercus libani	7.9 ± 0.9	6.8 ± 0.1	0.125 ± 0.013	10.8 ± 0.6
Minimum	6.4	5.8	0.0	5.2
Maksimum	36.8	10.2	0.2	13.8
Mean	21.5	7.9	0.1	8.7

Table 1. Continue

Fe	Mn	Ni	Zn
65.1 ± 3.9	9.6 ± 0.1	0.111 ± 0.100	3.3 ± 0.2
13.7 ± 1.0	1.7 ± 0.1	0.205 ± 0.203	2.5 ± 0.2
30.9 ± 0.7	7.2 ± 0.5	0.020 ± 0.034	3.4 ± 0.1
20.8 ± 1.8	6.4 ± 0.2	0.058 ± 0.101	14.6 ± 0.8
23.1 ± 0.6	3.3 ± 0.2	0.000 ± 0.000	8.3 ± 10.9
19.0 ± 0.9	4.3 ± 0.3	0.121 ± 0.181	16.0 ± 18.8
26.8 ± 0.9	4.9 ± 0.2	0.000 ± 0.000	10.6 ± 10.0
23.6 ± 0.9	6.7 ± 0.1	0.163 ± 0.226	6.5 ± 0.5
13.7	1.7	0.0	2.5
65.1	9.6	0.2	16.0
29.1	5.5	0.1	8.6

Table 2. Heavy metal and micro element concentrations of acorn fruits of oak (mg kg^{-1}; dw; Data are presented as means ± SD, n = 3 replicates)

Samples	Al	B	Cr
Quercus vulcania	5.3 ± 0.4	9.1 ± 0.3	0.034 ± 0.005
Quercus cerris var. cerris	9.0 ± 1.0	8.0 ± 0.1	0.113 ± 0.014
Quercus trojana	1.4 ± 0.3	5.9 ± 0.1	0.123 ± 0.015
Quercus coccifera	1.8 ± 0.3	5.4 ± 0.2	0.127 ± 0.001
Quercus pubescens	4.4 ± 0.6	6.8 ± 0.4	0.103 ± 0.009
Quercus ithaburensis ssp. macrolepis	4.0 ± 0.4	6.9 ± 0.1	0.136 ± 0.015
Quercus robur ssp. robur	10.8 ± 1.6	10.0 ± 0.7	0.088 ± 0.010
Quercus libani	0.5 ± 0.1	5.9 ± 0.1	0.092 ± 0.008
Minimum	0.5	5.4	0.034
Maksimum	10.8	10.0	0.136
Mean	5.2	7.4	0.098

Table 2. Continue

Cu	Fe	Mn	Ni	Zn
7.5 ± 0.3	35.2 ± 3.1	17.3 ± 0.4	0.265 ± 0.069	3.6 ± 0.2

9.2 ± 0.3	39.2 ± 0.8	18.2 ± 0.6	0.120 ± 0.113	3.3 ± 0.2
8.3 ± 0.4	17.5 ± 0.4	12.0 ± 0.1	0.272 ± 0.073	15.0 ± 1.5
8.7 ± 0.3	31.4 ± 0.8	43.1 ± 3.0	0.033 ± 0.043	12.6 ± 0.9
10.0 ± 0.4	19.1 ± 0.2	10.3 ± 0.3	0.000 ± 0.000	17.9 ± 1.8
5.5 ± 0.4	30.8 ± 0.6	11.9 ± 0.1	0.000 ± 0.000	5.6 ± 0.4
9.9 ± 0.7	25.1 ± 1.6	12.1 ± 0.1	0.180 ± 0.278	6.3 ± 0.4
7.8 ± 0.1	22.8 ± 0.9	11.6 ± 0.0	0.295 ± 0.089	13.9 ± 0.5
5.5	17.5	10.3	0.000	3.3
10.4	39.2	43.1	0.295	17.9
8.6	27.4	16.5	0.130	9.6

Table 3. Macro element concentrations of acorn fruits hulls of oak (mg kg^{-1}; dw; Data are presented as means ± SD, n = 3 replicates).

Samples	Ca	K	Mg	P
Quercus vulcania	3043 ± 195	5189 ± 228	324 ± 3	935 ± 27
Quercus cerris var. cerris	4222 ± 138	4552 ± 78	236 ± 13	902 ± 69
Quercus trojana	2484 ± 200	7762 ± 73	515 ± 33	862 ± 6
Quercus coccifera	3770 ± 111	1447 ± 66	357 ± 9	1066 ± 31
Quercus pubescens	3533 ± 378	5424 ± 121	401 ± 5	848 ± 68
Quercus ithaburensis ssp. macrolepis	2311 ± 122	6235 ± 234	287 ± 8	1274 ± 84
Quercus robur ssp. robur	1984 ± 30	5296 ± 105	741 ± 27	937 ± 67
Quercus libani	2646 ± 85	7173 ± 75	533 ± 5	1081 ± 17
Minimum	1632	1447	236	848
Maksimum	4222	7762	752	1274
Mean	2847	5204	461	9723

Table 4. Macro element concentrations of acorn fruits of oak (mg kg^{-1}; dw; Data are presented as means ± SD, n = 3 replicates).

Samples	Ca	K	Mg	P
Quercus vulcania	65 ± 3	9650 ± 74	469 ± 8	1150 ± 58
Quercus cerris var. cerris	423 ± 39	10905 ± 266	675 ± 13	1748 ± 123
Quercus trojana	15 ± 1	10957 ± 447	505 ± 16	1275 ± 95
Quercus coccifera	424 ± 19	10629 ± 195	651 ± 23	1132 ± 13
Quercus pubescens	278 ± 12	10853 ± 347	543 ± 15	1240 ± 49
Quercus ithaburensis ssp. macrolepis	105 ± 5	13445 ± 156	642 ± 32	1717 ± 31
Quercus robur ssp. robur	80 ± 6	12558 ± 199	435 ± 9	1519 ± 25
Quercus libani	150 ± 8	11953 ± 124	556 ± 2	1283 ± 55
Minimum	15	9650	391	1132
Maksimum	424	13445	675	1748
Mean	177	11347	541	1367

Table 5. Protein and ash contents of acorn hulls of oak (%)

Samples	protein	Kül
Quercus vulcania	9.9	1.14
Quercus cerris var. cerris	7.9	1.53
Quercus trojana	9.9	1.76
Quercus coccifera	9.1	1.19
Quercus pubescens	10.9	1.83
Quercus ithaburensis ssp. macrolepis	9.5	1.99
Quercus robur ssp. robur	12.0	1.75
Quercus libani	8.0	1.97
Minimum	7.9	1.1
Maksimum	12.0	2.0
Mean	9.7	1.6

Table 6. Protein and ash contents of acorn fruits of oak (%)

Samples	protein	Kül
Quercus vulcania	12.2	2.20
Quercus cerris var. cerris	14.2	2.70
Quercus trojana	11.8	2.50
Quercus coccifera	14.9	2.63

Quercus pubescens	12.6	2.21
Quercus ithaburensis ssp. macrolepis	14.5	2.70
Quercus robur ssp. robur	10.9	2.68
Quercus libani	15.6	1.08
Minimum	10.9	1.1
Maksimum	15.6	2.7
Mean	13.6	2.3

ACKNOWLEDGEMENT

This work was supported by Selçuk University Scientific Research Project (S.U.-BAP. Konya-Turkey).

REFERENCES

Aksoy, A., Şahin, U., Duman, F. 2000. *Rohinia pseudo-acacia* L. as a possible biomonitor of heavy metal pollution in Kayseri. *Turkish Journal of Botany* 24:279-284

Al-Jassim, R.A.M., Ereifej, K.I., Shibli, R.A., Abudabos, A. 1996. Oak acorn as energy source for growing Awassi lambs. Proceedings of the Twentieth Annual Meetin. Sept- Oct., 1996. Sydney, New South Wales 20:113-114.

Başlar, S., Kula, I., Doğan, Y., Yıldız, D., Ay, G. .2009. A Study of Trace Element Contents in Plants Growing at Honaz Daği- Denizli, Turkey. *Ekoloji* 18:72,1-7.

Bouderoua, K. and G. Selselet- Attou. 2003. Fatty acid composition of abdominal adipose tissue in broilers fed green-oak(*Quercus ilew*), cork oak acorn (*Quercus suber* L.) based diets. *Animal Research* 52:377-382.

Cayir, A., Coşkun, M., and Coskun,M. 2008. Concentrations of some elements in the bioindicator organism *Cladonia rangiformis* collected at the vicinity of Canakkale. *Ekoloji* 18:69,7-13.

Davis, P.H. 1982. Flora of Turkey and the East Aegean Islands. Vol.7,Edinburgh University Pres.

Griffiths, D.W., Jones, D.I.H. 1977. Cellulase inhibition by tannin in the testa cellulase inhibition by tannin in the testa of field beans (*Vicia faba*). *Journal of the Science and Food Agriculture* 28:983-989.

Jhonston, W.R., J. Proctor. 1977 Metal concentrations in plants and soils from two British serpentine sites. *Plant Soil* 46:275-278.

Kaya, G., and Yaman, M. 2008. Trace Metal Concentrations in Cupressaceae Llaves as Biomonitors of Environmental Pollution. *Trace elements and Electrolytes* 25: 156-164

Kekos, D., Kaukios, B. 1985. Acid hydrolysate of acorn polysacharid as substrates of *Candida utilisis* growth. Biotechnology Letter 7:345-348.

Ng, O., H., Tna, B.C., Obbard, J.P. 2005. Lichens As Bioindicators of Atmospheric Heavy Metal Pollution In Singapore. *Environmental Monitoring and Assessment* 123: 63-74.

Ofcarcik, R.P. and Burns, E.E. 1971. Chemical and physical properties of selected acons. *Journal of the Science and Food Agriculture* 36:576-578.

Özcan, T., Bayçu, G. 2005. Some elemental concentrations in the acorns of Turkish *Quercus* L. (Fagaceae) Taxa. *Pakistan Journal of Botany* 37(2): 361-371.

Püskülcü,H., Ikiz,F.1989. Introdiction to Statistic. Bilgehan Presss, p 333, Bornova,Izmir, Turkey.(in Turkish)

Rababah, T.M., Ereifej, K.I., AL-Mahasneh, M.A., Alhamad, M.N., Alrababah, M.A., Muhammad, A.H. 2008. The Physicochemical Composition of Acorns for Two Mediterranean *Quercus* Species . *Jordan Journal of Agricultural Sciences* **4**:131-137

Rana, T., Gupta, S., Kumar, D., Sharma, S., Rana, M. Rathore, V.S., B.M.J. Raso, P.U., Deosthale, Y.G. 1982. Tannin Content of Pulse: Varietal Differences and Effect of Germination and Cooking. *Journal of the Science and Food Agriculture* 33:1013.

Rana, T., Gupta, S., Kumar, D., Sharma, S., Rana, M. Rathore, V.S., Pereira, B.M.J. 2004. Toxic effects of pulp and paper-mill effluents on male reproductive organs and some systemic parameters in rats. *Environmental Toxicology and Pharmacology* 18:1-7.

Skujins, S. 1998. Handbook for ICP-AES (Varian-Vista). A hort Guıde To Vista Series ICP-AES Operation.Varian Int.AGşZug.Version 1.0. pp 29. Switzerland.

Tanguy, J.M., Guillaume, J., Kossa, A.1977. Condensed Tannin in Horse Bean Seed. *Journal of the Science and Food Agriculture* 28:757

Yıldız, D., Kula, I., Ay, G., Başlar, S., Doğan, Y. 2010. Determination of trace elements in the plants of Mt. Bozdağ, İzmir, Turkey. *Archives of Biological Sciences* Belgrade, 62(3):733-740.

Yorek, N., Aydin, H., Ugulu, I., Doğan,Y. 2008. An Investigation on Students Perceptions of Biodiversity. *Natura Montenegrina* 7(3):165-173.