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RESEARCH ARTICLE

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Effect of cultivar and year of harvest on the mineral composition of Algerian extra-virgin olive oils

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Abstract

Aim of study: To evaluate the effect of cultivar and year of harvest on the content of mineral elements of Algerian extra virgin olive oils.

Area of study: Technical Institute of Arboriculture of Fruits and Vine (TIAFV), Bejaia, Algeria.

Material and methods: The mineral contents of extra virgin olive oils from ten cultivars during two consecutive campaigns 2014/2015 and 2015/2016 were determined using atomic absorption spectrometry and absorption in a graphite furnace after microwave-assisted acid digestion. Principal component analysis was applied to correlate the mineral content with cultivar type and year of harvest.

Main results: Mean concentrations for Fe, Zn, Cu, Na, K, Mg, As and Co in samples were observed in the range of 1.640-13.213, 1.546-32.866, 1.375-3.337, 19.666-104.720, 4.573-117.133, 0.120-2.560, 0.006-0.146 and 0.002-0.051 $\mu g\ g^{-1}$, respectively. The first three principal components retained 76.25% of the variance. The determinants of the effect of cultivar type and year of harvest were Fe and Na; Mg, Co and As, respectively.

Research highlights: The study showed that mineral composition of the olive oils was mainly determined by the cultivar and the year of harvest.

Additional key words: atomic absorption; campaigns; microwave; principal components analysis.

Abbreviations used: FAAS (flame atomic absorption spectroscopy); GFAAS (graphite furnace atomic absorption spectrometer); MI (maturation index); PCA (principal component analysis).

Authors' contributions: SK and ZS: olive harvest and extraction. KBH and LB: Oil analysis. KBH: drafting of the manuscript. HB and KBH: Statistical analysis. All authors read and approved the final manuscript.

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Introduction

Olive (*Olea europaea* L.) cultivation is very important for many countries, especially those in the Mediterranean basin, for historical, ecological and economic reasons (Chatzistathis *et al.,* 2012). Olive oil consumption has been directly associated with the protection of cardiovascular health and the prevention of cancer and neurodegenerative diseases, which supports the recommendation for its consumption (Rincon-Cervera *et al.*, 2016). The benefits have been associated with a high content of monounsaturated fatty acids (MUFA) and minor components, particularly phenolic compounds (Angelis *et al*., 2017).

In Algeria, the olive tree is the main fruit species and plays a very important socio-economic role. Since 2000 olive cultivation has undergone profound changes and expansion following the implementation of several development programs. As a consequence, agricultural surfaces devoted to this crop has increased from 150,000 to 500,000 hectares nationwide. Indeed, the development of the olive sector is linked not only to the extension of the areas planted and to the increase in productivity, but also to the preservation and improvement of quality.

Quality control of vegetable oils is dominated by the determination of certain classical parameters such as acidity, peroxide concentration, fatty acid composition and phenolic compounds. Nevertheless, the determination of the element content of vegetable oils is an important criterion for assessing the quality of oils with regard to freshness, conservation properties, storage and their influence on nutrition and human health (Nunes *et al.*, 2011). The presence of certain element species, such as Cu, Co, Fe, Mg, Mn, Zn and Ni, can promote the oxidative degradation of the oil even at low concentrations (Bakircioglu *et al.,* 2013). The oxidative process may increase some carcinogenic effects and develop pathological effects on the digestive system (Llorent-Martinez *et al.,* 2011; Zhu *et al.,* 2011). Other element species, such as As, Cd, Hg and Pb are potentially toxic for human consumption, depending on their concentration in oil (Bakircioglu *et al.,* 2013; Ni *et al.,* 2016).

The mineral content of vegetable oils depends on several factors; they can be incorporated into oil from the soil although their concentrations are modulated by the biochemical pathways of each cultivar (Chatzistathis *et al.,* 2009). They arrive in the olive plant by deposition as well as by bioaccumulation in the soil due to natural sources of metals and environmental pollution (Zeiner *et al.,* 2005). Moreover, the composition of olive oil can vary from one season to another according to climatic variations. Many studies have been carried out on the influence of climatic variations on the quality of olive oil; precipitation and temperature are the most important environmental factors that can influence oil composition (Romero *et al.,* 2003; Agiomyrgianaki *et al.,* 2012; Mansouri *et al.,* 2018). In addition to these facts, agronomic techniques such as fertilizer use and irrigation, and the collection of olive, as well as the process of oil extraction play an important role. Metals can also be introduced during the production process or by contamination of metal processing equipment and thus be suspended in the oil (Dugo *et al.,* 2004).

Atomic absorption spectrometry is still the most commonly used technique for determining concentrations of mineral elements in olive oil, such as flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS), as well as inductively coupled plasma optical emission and mass spectrometry (ICP-OES and ICP-MS) (Mendil *et al.,* 2009; Zhu *et al.,* 2011; Llorent-Martínez *et al.,* 2014). Most spectroscopic techniques require sample pre-processing. The microwave digestion system for laboratory applications has offered enormous advantages in mineralization (Ansari *et al.,* 2009).

Algerian olive oils have been characterized by their phenolic profile and antioxidant potential (Soufi *et al.,* 2018) as well as by their volatile organic compounds (Cherfaoui *et al.,* 2018). However, to our knowledge, the mineral composition of Algerian olive oil has not yet been evaluated. The objective of this study was therefore to determine the concentrations of iron, zinc, copper, potassium, sodium, magnesium, arsenic and cobalt in olive oils from ten Algerian olive cultivars grown in Sidi-Aïch (Bejaia) and to evaluate the effect of cultivar and harvest on mineral composition.

Material and methods

Experimental design

The trials were carried out on Algerian extra monovarietal extra virgin olive oils of ten cultivars (Limli, Ferkani, Chamlel, Abani, Zeletni, Souidi, Bouricha, Aalah, Rougette de Mitidja and Mekki), obtained from a collection of the Technical Institute of Arboriculture of Fruits and Vine (TIAFV), located in the Soummam Valley (Sidi-Aïch, Bejaia, Algeria), central-eastern region of Algeria about 1 km from the national road 26.

The olive trees were grown under identical agronomic and pedoclimatic conditions. The selected olive trees were over 60 years old planted at 10×10 m and harvested by hand during the 2014/2015 and 2015/2016 seasons, from late December to early January, due to the different maturation periods of the different cultivars [maturation index (MI) ranging from 2.01 to 3.30]. Olive trees were subjected to non-irrigated conditions throughout the year, except during July and August, when trees were irrigated (50 L/m^2 per tree) once a week. Monthly precipitation from 2014 to 2016 for the study area is shown in Fig. 1. In the spring, foliar fertilizers were applied to stimulate growth shoot.

After harvesting, the olives were immediately transported to the laboratory in plastic crates. The olive oil was extracted separately from each cultivar using an oleodoseur Siol 20240 (Ghisonaccia, France) equipped with a centrifugal divider (48000 rpm) with a capacity of 1.5 kg. The olives were crushed using a hammer mill and the resulting paste was mixed in an olive paste blender at room temperature for 40 min. The olive oil was then separated by centrifugation without the addi-

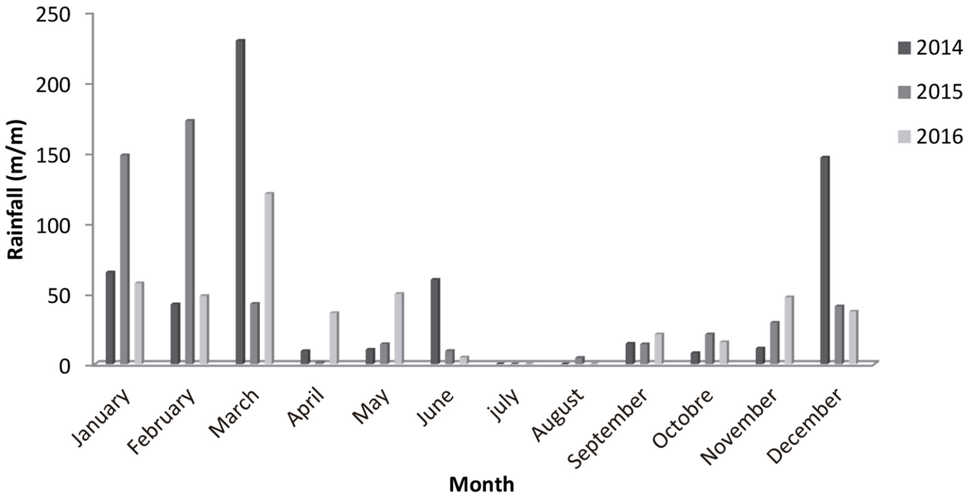


Figure 1. Monthly rainfall data for the study area from 2014 to 2016.

tion of hot water using a two-phase decanter. The resulting oils were packaged in dark glass bottles and stored at -20 °C until analysis.

Reagents and glassware

In this work, ultrapure water from a Milli-Q system (Millipore, Milford, MA) was used to prepare all solutions. All reagents and standard stock solutions used were from Merck (Darmstadt, Germany). For digestion preparation, nitric acid (65%) and hydrogen peroxide (30%) were employed. To reduce the risk of contamination, all laboratory glassware was soaked in 10% v/v HNO_3 for at least 24 h and then rinsed copiously with ultrapure water before use.

Apparatus and instruments

An Agilent 240FS AA Fast Sequential atomic absorption spectrometer (FAAS) was used for the determination of Zn, Fe, K, Na and Mg. As, Co and Cu were analyzed by GFAAS, an Agilent 240Z AA Zeeman graphite furnace atomic absorption spectrometer was used for graphite furnace measurements. The operating conditions for FAAS and GFAAS are presented in Table 1 and Table 2, respectively. The samples were digested using a microwave-assisted digestion (Milestone Ethos MicroSYNTH) oven with programmable power control (10W increments, maximum power 1000 W) with segmented rotor MPR-600 (35 bar of maximum operating pressure and 260°C of maximum operating temperature) and 10 reaction vessels.

Microwave-assisted acid digestion

Triplicate samples of olive oil samples from each cultivar were weighed (0.5 g) and added into the digestion vessel with 7 mL of nitric acid and 1 mL of hydrogen peroxide. Then, the samples were digested in a microwave digester using a two-step temperature program. In the first step, the temperature was linearly increased to 200 °C over 10 min; the maximum power of

Table 2. Instrumental parameters for metal determination by GFAAS.

Element	As	Cu	Co
Wavelength (nm)	193.7	324.8	240.7
Pretreatment temperature (ºC)	1400	800	750
Atomization temperature (ºC)	2600	2300	2300

Table 1. Instrumental parameters for metal determination by FAAS.

Element	Fe	Zn	Mg	Na	K
Wavelength (nm)	248.3	213.9	285.2	589.0	766.5
Slit width (nm)	0.2	1.0	0.5	0.5	1.0
Lamp current (mA)	5.0	5.0	4.0	5.0	5.0
Acetylene flow (L/min)	13.50	13.50	13.50	13.50	13.50
Fuel gas (L/min)	2.00	2.00	2.00	2.00	2.00

the rotating magnetron was 1000 W. In the second step, the temperature was maintained at 200 °C for 15 min. After digestion and cooling at room temperature, all the digestion liquors were diluted with ultrapure water in a 20 mL volumetric flask. Prior to analysis by FAAS and GFAAS each sample was vigorously shaken.

Calibration procedure

For the quantitative analysis of oils, all calibration curves were built from standards at five different concentrations. The element standards solutions were prepared by diluting stock standards for each element (1000 mg/L) in a nitric acid solution (1% v/v). Calibration ranges were selected according to the expected concentrations of the elements of interest.

Statistical analysis

The results of the mineral composition were expressed as a mean value ± standard deviation. The statistical analysis was carried out using SPSS 21 statistical package program. Two-way ANOVA was employed to find the significant differences of mineral elements contents in ten cultivars of olive oils with respect to cultivar and year of harvest. The significant differences were set at $p<0.05$. Mineral elements' data was analyzed through principal component analysis technique (PCA), using XLSTAT version 19.3.01.

Results and discussion

The results of two-way ANOVA and the elemental concentrations with standard deviations (SD) in the ten olive oil cultivars analyzed for two distinct years of harvest (2014/2015 and 2015/2016) are summarized in Table 3 and Table 4, respectively. Among all determined mineral elements, Na and K were found to be the dominant elemental ion, followed by Fe. Two–way ANOVA test showed that the amounts of minerals in the samples olive oils were significantly affected by the cultivar and the year of harvest as well as the interaction between these two factors. However, the cultivar did not show any significant effect on iron levels.

Distribution of Fe, Zn, Cu, Na, K, Mg, Co and As in olive oil samples

Macro minerals play an important role in various bodily functions. Sodium is the main cation in extracellular fluid in the body, the recommended daily intake for Na is 2 g/day (equivalent to 5 g salt/day) (WHO, 2007). Na concentrations in our samples were high in the 2014/2015 season samples. This trend was particularly relevant for the cultivar Rougette de Mitidja, which had the highest value at 104.720 µg g^{-1}. The Na levels in olive oil samples were higher than in previous reports (Mendil *et al.,* 2009; Zeiner *et al.,* 2010). However, concentrations were lower than these literature values 73.401-390.699 µg g^{-1} (Fuqha *et al.,* 2015), 110-320 µg g^{-1} (Gouvinhas *et al.,* 2015) and 150-200 µg g^{-1} (Gouvinhas *et al.,* 2016).

Relevant to the Na concentrations, Mg levels for the 2014/2015 season (1.040-2.560 µg g^{-1}) were also higher than those for 2015/2016 season (0.120-0.560 µg g^{-1}). In other works by Zeiner *et al.* (2005) and Fuqha *et al.* (2015), the concentration of Mg ranged 2.910-3.620 and 294.738-782.968 µg g^{-1} respectively.

In contrast to Na and Mg, the concentrations of K in our samples from 2015/2016 season were relatively higher than those of the corresponding samples from the 2014/2015 season. The highest value (117.133 µg g^{-1}) was observed in cv. Aalah. WHO (2012) suggests a K intake of at least 90 mmol/day (3510 mg/day) for adults. The values of K from the present study were higher than those reported by Mendil *et al.* (2009) and Zeiner *et al.* (2010), with the exception of the Fuqha *et al.* (2015), who reported a higher value of 168.883 µg g^{-1}.

In fact, the year of harvest had a significant influence on Na, Mg and K levels. The increase in Na and Mg concentrations and the decrease in K concentrations obtained in the 2014/2015 season, whereas the opposite was observed in the 2015/2016 season, is probably the result of the interactions between minerals. These interactions can be modulated by environmental and agronomic conditions such as precipitation, irrigation in summer and foliar fertilizers; salts in water can have an influence on plant growth and, therefore, on the efficiency in nutrient use. It is well known that K, Ca and Mg interact in the soil exchange complex, sometimes inducing deficiencies in one element through an excess of another. Interactions also occur at the plant level, *e.g.* a deficiency or excess of one element may affect the uptake or utilization of another (Fernández-Escobar *et al.,* 2019). The concentration of NaCl in the soil can interfere with the absorption of cations such as K^+ (Tester & Davenport, 2003) and excessive amounts of K reduce Mg absorption (Guo *et al*., 2016). Lower K concentrations compared to Na concentrations have been reported in olive root and fruit (Bedbabis *et al.,* 2014).

Table 3. Mean (μg g-1) and standard deviation of elements detected from ten cultivars of olive oils during two consecutive olive crop seasons (2014/2015 and 2015/2016).

Element	Season	Limli	Aalah	Mekki	Chamlal	Bouricha
Fe	2014/2015	13.213±0.560	8.146±1.377	11.733±0.729	8.693±1.447	7.080±0.417
	2015/2016	9.546±0.921	7.920±1.076	8.386±0.234	5.586±1.882	13.200±0.491
Zn	2014/2015	4.00±0.346	4.266±0.780	1.813±0.582	3.626±0.921	8.386±0.833
	2015/2016	2.666±0.234	15.146±1.082	8.64±0.174	22.546±1.963	14.506±0.140
Cu	2014/2015	1.474±0.0238	1.375±0.146	1.383±0.014	1.427±0.032	1.465±0.027
	2015/2016	3.109±0.455	2.214±0.094	1.720±0.104	2.774±0.295	2.359±0.758
Na	2014/2015	51.546±2.014	56.733±5.771	47.333±1.830	57.48±3.402	50.973±2.326
	2015/2016	23.106±0.496	25.973±2.079	20.72±0.240	19.666±0.371	20.933±0.100
K	2014/2015	20.720±2.751	8.173±0.620	4.84±0.454	10.693±2.670	8.226±0.582
	2015/2016	66.986±0.483	117.133±1.842	14.706±0.410	27.32±0.327	26.933±0.323
Mg	2014/2015	2.560±0.222	1.32±0.080	1.146±0.257	1.826±0.305	2.040±0.243
	2015/2016	0.240±0.040	0.546±0.023	0.253±0.023	0.560±0.000	0.293±0.023
Co	2014/2015	0.1468±0.038	0.101±0.016	0.083±0.003	0.094±0.003	0.057±0.008
	2015/2016	0.029±0.007	0.006±0.004	0.053±0.008	0.028±0.002	0.042±0.007
As	2014/2015	0.003±0.001	0.007±0.001	nd	nd	0.004±0.001
	2015/2016	0.051±0.011	0.042±0.014	0.049±0.009	0.032±0.013	0.007±0.003

Table 3. (cont.).

Element	Season	Abani	Zeletni	Rougette de Mitidja	Ferkani	Souidi
Fe	2014/2015	1.880±0.529	2.973±1.420	9.680±2.24	1.640±0.405	3.146±1.171
	2015/2016	3.626±0.508	2.586±0.680	7.320±0.400	7.226±0.568	7.026±0.593
Zn	2014/2015	1.546±0.369	4.520±0.969	5.386±1.346	5.266±1.160	7.946±0.843
	2015/2016	8.866±0.234	8.493±0.100	9.786±0.647	32.866±1.454	1.773±0.061
Cu	2014/2015	1.467±0.009	1.508±0.052	2.558±0.419	1.440±0.013	1.702±0.036
	2015/2016	1.689±0.087	3.337±0.759	1.925±0.110	1.867±0.035	2.307±0.491
Na	2014/2015	57.493±3.265	51.466±1.937	104.72±13.747	66.693±1.889	67.880±3.028
	2015/2016	23.680±0.120	20.493±0.128	20.973±0.614	21.866±0.266	23.160±0.423
K	2014/2015	5.680±0.280	4.573±0.220	10.373±0.843	5.773±0.551	8.893±0.980
	2015/2016	14.106±0.333	9.946±0.272	43.586±0.601	10.48±0.341	20.666±0.302
Mg	2014/2015	1.040±0.080	1.266±0.323	2.013±0.438	1.053±0.083	1.600±0.120
	2015/2016	0.213±0.023	0.240±0.000	0.240±0.040	0.44±0.000	0.120±0.000
Co	2014/2015	0.087±0.009	0.055±0.006	0.106±0.012	0.049±0.004	0.042±0.008
	2015/2016	0.038±0.002	0.025± 0.007	0.050±0.027	0.055±0.025	0.033±0.021
As	2014/2015	0.005±0.001	0.003±0.000	nd	0.002±0.001	0.012±0.002
	2015/2016	0.008±0.001	0.008±0.005	0.002±0.001	0.005±0.001	0.008±0.001

nd: not detected.

Table 4. Two-way ANOVA results for cultivars and year of harvest as grouping variables.

Source of variation	Dependent variable	SS	DF	MS	F	Sig.
Cultivar	Fe	526.961	9	58.551	55.061	0.000
	Zn	1254.227	9	139.359	182.222	0.000
	Na	5.127	9	0.570	5.897	0.000
	K	4065.676	9	451.742	33.328	0.000
	Mg	36274.791	9	4030.532	1354.661	0.000
	As	3.572	9	0.397	13.124	0.000
	Cu	0.014	9	0.002	6.965	0.000
	Co	0.006	9	0.001	11.649	0.000
Season	Fe	2.697	1	2.697	2.536	0.119
	Zn	925.123	1	925.123	1209.669	0.000
	Na	8.538	1	8.538	88.386	0.000
	K	21842.784	1	21842.784	1611.509	0.000
	Mg	1360.980	1	1360.980	457.425	0.000
	As	24.270	1	24.270	802.571	0.000
	Cu	0.032	1	0.032	145.254	0.000
	Co	0.004	1	0.004	65.710	0.000
Cultivar* Season	Fe	187.559	9	20.840	19.598	0.000
	Zn	1251.042	9	139.005	181.759	0.000
	Na	7.308	9	0.812	8.406	0.000
	K	4042.158	9	449.129	33.136	0.000
	Mg	10000.604	9	1111.178	373.467	0.000
	As	4.054	9	0.450	14.896	0.000
	Cu	0.020	9	0.002	10.332	0.000
	Co	0.004	9	0.000	8.205	0.000
Corrected model	Fe	759.752	59			
	Zn	3460.982	59			
	Na	24.837	59			
	K	30492.788	59			
	Mg	47755.386	59			
	As	33.105	59			
	Cu	0.075	59			

SS: type III sum squares. DF: degrees of freedom. MS: mean square. F: F-ratio.

Elemental ions such as Cu, Fe and Zn are involved in many crucial biological processes and are necessary for the survival of any living organism. Although, many reports describe the deleterious effect of trace amounts of elements on the oxidative stability of oils, Fe, Ni and Co in particular, significantly reduce the oxidative stability of unsaturated fats and accelerate the development of rancidity in edible oils and fats when their concentration is a few ppm (Angerosa & Di Giacinto, 1993).

Regarding the elemental analysis, the quantities of Cu detected ranged from 1.383 to 3.337µg g^{-1}. Oils harvested in the second year had higher Cu concentrations than those harvested in the 2014/2015 crop year. With the exception of 'Zeletni', which has the highest value in the first crop year. Our values were in agreement with some publications (Fuqha *et al.,* 2015). However, any sample we analyzed exceeded the maximum limit of 0.1 mg/kg set by the International Oil Council (IOC, 2015) in virgin olive oils.

In addition, our results showed a high variability in Fe content in the first and second crop years. For all cultivars, levels of Fe were higher in the first year than in the second, except for 'Bouricha', 'Abani', 'Ferkani' and 'Souidi'. Our results (1.640-13.213 µg g^{-1}) were higher than those obtained by Pehlivan *et al*. (2008) (0.0125-0.0295 µg g^{-1}) and by Zeiner *et al.* (2010) (0.05-4.61 µg g^{-1}), but close to those of Mendil *et al.* (2009) (52.0-291.0 µg g^{-1}) and Zhu *et al.* (2011) (32.8-34.1 µg g^{-1}).

In accordance with Fe, large variations were also observed for Zn between cultivars for the same crop year and between both crop years. The highest concentrations were present in the samples of olive oils harvested in the 2015/2016 crop (2.666-32.866 µg g^{-1}). Our results were higher than those of other studies

(Beltrán *et al.,* 2015) but close to those of Fuqha *et al.* (2015) which were about 13.743 and 116.658 µg g^{-1}.

The variation in Cu, Fe and Zn contents was influenced by both type of cultivar and year of harvest. In relation to the type cultivar, the olive trees are grown in the same area, so they have been exposed to the same soil and climatic conditions, and extraction conditions were the same for all cultivars. However, in the same crop season mineral contents differences in olive oil were observed, which could be explained by the genotype.The genotype can influence growth rate directly, or indirectly through its influence on nutrient utilization efficiency (Chatzistathis *et al.,* 2012); for example, according to Nergiz & Engez (2000), cultivar properties influence the iron levels in olive fruit. Seasonal differences could be explained by environmental and agronomic factors; the presence of discharging waste from industrial and domestic sources into the Soummam River, which is not far from the study area, appears to have effect on Cu, Fe and Zn concentrations. Mouni *et al.* (2009) showed significant concentrations on Fe in water samples from the Soummam River. Indeed, the work of Gouvinhas *et al.* (2016) on olive oils from three major Portuguese cultivars ('Galega', 'Cobrançosa' and 'Picual') at different stages of ripening showed that the main variations in mineral content affect Fe, Zn and Cu. In addition, Angioni *et al.* (2006) showed high variability within cultivars and with the first and second harvests for Zn.

The FAO/WHO (1999) has set a limit for elements intakes based on body weight. For an average human adult (60 kg body weight), the provisional daily intake (PTDI) for Cu, Zn and Fe are 3 mg, 60 mg, and 48 mg, respectively. Regarding the bioavailability of trace elements, rats fed with an olive-oil supplemented diet had significantly lower levels of serum iron and transfertin saturation than control (Chetty *et al.,* 1999), while Zn and Mg concentrations in mice tissue remained unchanged (Milin *et al.,* 2001).

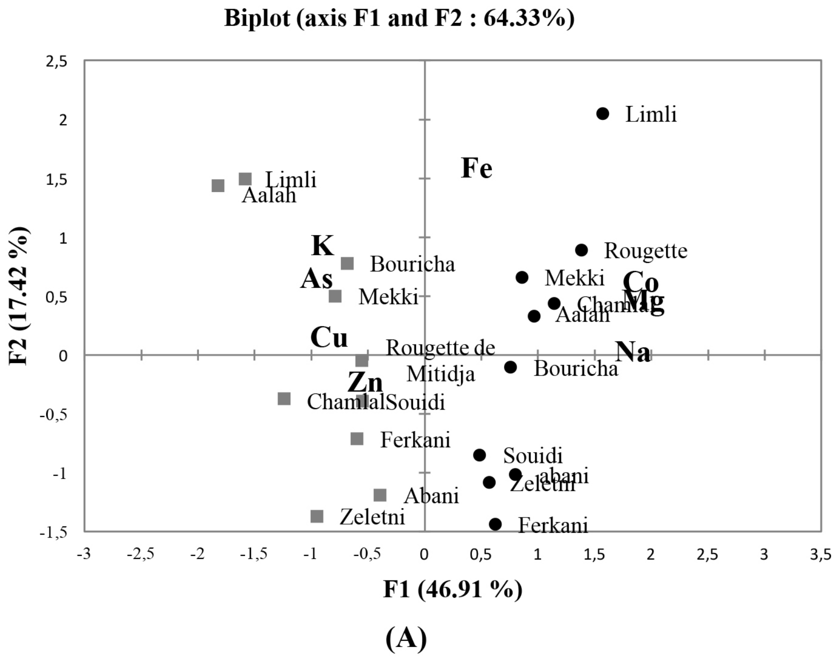
The determination of trace and toxic heavy metal concentrations in food is a major concern in public health studies. As far as Co is concerned, this element is beneficial to humans because it is part of vitamin B12, which is essential for maintaining human health. Cobalt (0.16-1.0 mg cobalt/kg body weight) was also used as a treatment for anemia (Agency for the Toxic Substances and Disease Registry (ATSDR, 2004). Nevertheless, based on animal data on acute and chronic exposure to Co, the International Agency for Research on Cancer (IARC) has determined that it is possibly carcinogenic to humans (ATSDR, 2004). The Co content of the samples ranged from 0.006 to 0.146 µg g^{-1}. These values are lower than those previously reported by Mendil *et al.* (2009) (1. 3 µg g^{-1}).

Inorganic forms of As such as arsenite and arsenate are more dangerous to human health. They are highly carcinogenic and can cause lung, liver, bladder and skin cancer. Humans are exposed to arsenic through air, food and water (Jaishankar *et al.,* 2014). The highest As content in our oil samples was found in Limli (0.051 µg g^{-1}), the presence of this element could be due to environmental contamination. It should be noted that the study area is located 1 km from National Highway 26, which is considered one of the busiest traffic roads in Algeria, with vehicular traffic polluting the road environment and neighboring agricultural land with a range of contaminants. Heavy metals are found in fuels, fuel tanks, engines and other vehicle components, catalytic converters, tires and brake pads, and road surfacing materials (Zehetner *et al.,* 2009). According to Yan *et al.* (2013), the rank of risk contribution to environments among the eight heavy metals studied was Cd > As > Ni > Pb > Pb > Pb > Cu > Co > Zn > Cr. Indeed, Madejón *et al.* (2006) observed the presence of As in olives produced in the Guadiamar Valley (southwest Spain), which was polluted by a spill from an open pit pyrite mine.

Chemometric analysis

Chemometric tools were applied to all data. PCA made it possible to group the variables on the basis of mutual correlations and to group the samples according to their similarities. The mean values (n = 3) of the elements detected (Fe, Zn, Cu, Na, K, Mg, As, Co) were used as variables to perform an exploratory analysis using PCA. The first three principal components were selected; they accounted for more than 76.25% of the total variation. Principal components 1, 2, and 3 explained 46.91, 17.42 and 11.92% of the total variance, respectively; they effectively characterize the mineral elements in the cultivars. The variables with the highest absolute load value on the principal component 1 were Mg, Na, Co and As, while for principal component 2, Fe and K had a higher load, and for the principal component 3, Zn are most important. The interrelations between the elements are most evident in the projections of components 1 and 2, and 1 and 3 (Fig. 2A and Fig. 2B, respectively).

A loading plot for the PC1 and PC2 plane and the PC1 and PC3 plane (Fig. 2A and Fig. 2B) allowed a good separation of oils obtained from the olives during the 2014/2015 and 2015/2016 seasons, which is mainly determined by the concentration of the elements Mg, Na, Co and As.



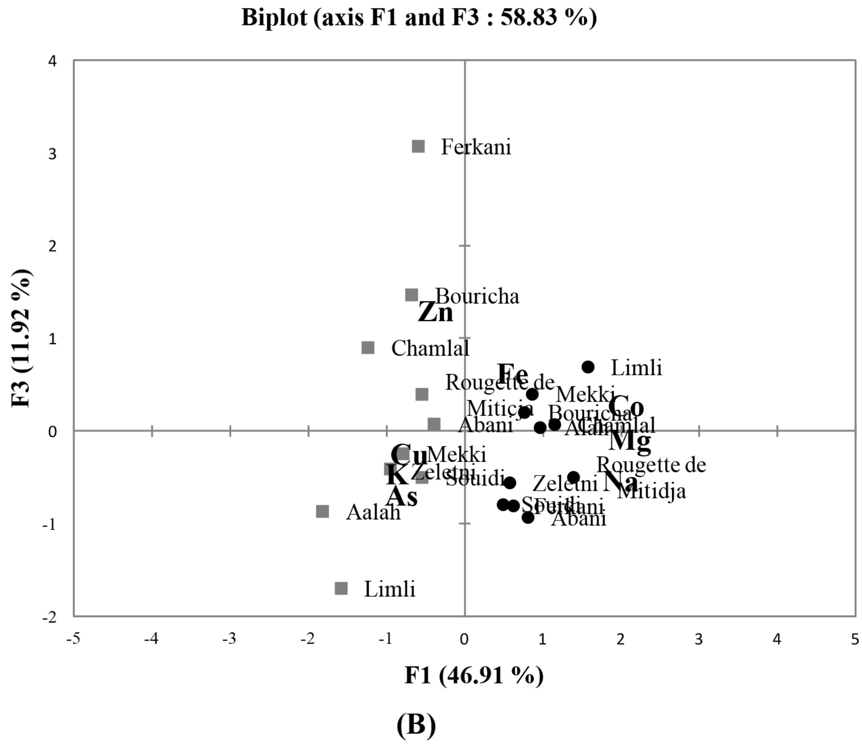


Figure 2. Bivariate plot for the first three PCs. Samples are identified according to the cultivar and year of harvest. (A): loadings plot for PC1 and PC2; (B) loadings plot for PC1 and PC3 (■ crop season 2014/2015 ● crop season 2015/2016).

According to the Fig. 2A, there is a negative correlation between the elements Mg, Na, Co and the toxic metal As. It is clear that the concentration of these elements is strongly linked to the agro-climatic conditions and consequently to the specific season on which the olives were harvested. In the score plot generated by combining principal components 1, 2 (Fig. 2A), Fe was the element that contributed most to the categorization with distinct cultivars included in this study. PC2 therefore reflects the particularity of the 'Limli' cultivar, in terms to its composition, which is strongly composed of Fe during the two harvest years. In PC1 and PC3 (Fig. 2B), the high Zn concentrations of 'Bouricha' and 'Zeletni' cultivars are responsible for the high score of the third component.

For the first time, this study reports mineral composition of Algerian monovarietal olive oils, obtained from two consecutive crop seasons, 2014/2015 and 2015/2016. The obtained results demonstrate that the combination of experimental data and chemometric technique can be used to distinguish olive oils samples according to cultivar and year of harvest. Fe is the element that contributes most to the categorization of cultivars, while Na, Mg, Co and As are the major elements that are strongly related to local agricultural and environmental conditions and therefore determine the crop season.

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