

Isotopic and Elemental Data for Tracing the Origin of European Olive Oils

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H, C, and O stable isotope ratios and the elemental profile of 267 olive oils and 314 surface waters collected from 8 European sites are presented and discussed. The aim of the study was to investigate if olive oils produced in areas with different climatic and geological characteristics could be discriminated on the basis of isotopic and elemental data. The stable isotope ratios of H, C, and O of olive oils and the ratios of H and O of the relevant surface waters correlated to the climatic (mainly temperature) and geographical (mainly latitude and distance from the coast) characteristics of the provenance sites. It was possible to characterize the geological origin of the olive oils by using the content of 14 elements (Mg, K, Ca, V, Mn, Zn, Rb, Sr, Cs, La, Ce, Sm, Eu, U). By combining the 3 isotopic ratios with the 14 elements and applying a multivariate discriminant analysis, a good discrimination between olive oils from 8 European sites was achieved, with 95% of the samples correctly classified into the production site.

KEYWORDS: Olive oil; European origin; traceability; IRMS; ICP-MS

INTRODUCTION

On February 4, 2009, the European Union (EU) Member States agreed to compulsory origin labeling for virgin and extra virgin olive oils (EC Regulation 182/2009) to avoid consumers being misled about their true characteristics and origin. This highlights the increasing demand for analytical methods and statistical tools capable of effectively verifying claims of origin.

The stable isotope ratios of bioelements, as well as the elemental profile, measured by isotope ratio mass spectrometry (IRMS) and inductively coupled plasma–mass spectrometry (ICP-MS) have been shown to be useful markers for tracing the geographical origin of several foods, including olive oils (1–5).

The H, C, and O isotopic composition of olive oils and of plant material in general is related to the climatic conditions (relative humidity, temperature, amount of precipitation) and geographical characteristics (distance from the sea or other evaporation source, altitude, latitude) of the area where the plants grow (6–9) and to the plant variety (3). The ¹³C/¹²C ratios of plant compounds are affected by the botanical origin of the plant (discrimination between C3 and C4 plants) (10) and by several environmental and physiological factors that influence the

stomatal conductance and the intercellular and ambient CO₂ concentration, such as relative humidity, temperature, amount of precipitation, water stress, plant age, and maturation (8, 11–14). The ²H/¹H and ¹⁸O/¹⁶O ratios of plant material reflect (a) the ratios of water uptake by the plant (linked to latitude, elevation, distance from the evaporation source, temperature, and amount of precipitation) (15, 16), (b) the evaporative and diffusional effects during transpiration (affected by relative humidity, temperature, isotope composition of water vapor) (9, 17), and (c) the biosynthetic pathways including the isotopic exchange between organic molecules and plant water (17–19).

The elemental content of plants is mainly related to the geological and pedoclimatic characteristics of the site of growth (20). Vegetable-derived manufactured products such as olive oil will have a trace element content related not only to that of soil but also to farming, olive collection, manufacturing, refining, and storage processes (21–23).

Within the framework of the European TRACE Project, 267 olive oils collected from eight European sites were analyzed for H, C, and O stable isotope ratios and their elemental profiles. H and O isotope ratios and elemental composition were also measured in 314 fresh surface waters from the same sites. The aim of the study was to investigate if olive oils produced in areas with different climatic and geological characteristics could be discriminated on the basis of isotopic and elemental data.

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This capability was also tested in relation to the composition of the corresponding surface waters.

To our knowledge, such a multielement and multi-isotopic study on the traceability of authentic European olive oils and of the related source surface waters has never been reported, thus far.

MATERIALS AND METHODS

Samples. Two hundred and sixty-seven European extra virgin olive oils were collected at the mill from the milling of multivarietal olives from 8 European sites during the 2005 and 2006 harvests. At the 8 sites, also 314 surface waters were sampled during all four seasons of 2005 (Table 1). The mean values of 5 month temperature (°C), relative humidity (%), and 5 month total amount of rainfall (mm) were taken from the closest weather station: Web sites <http://www.meteotrentino.it>, Arco (TRE); <http://www.ilmeteo.it/>, Sesto Fiorentino (TOS) and Assoro/Enna (SIC); <http://www7.ncdc.noaa.gov/>, Faro/Almanacil (ALG) and Carpentras (CAR); the Servei Meteorològic de Catalunya, Barcelona (BAR); the Hellenic National Meteorological Service through Prof. Michael Komaitis (Agricultural University of Athens, Greece), Mikra (CHA), and Kalamata/Gythi (LAK). When not available (CHA, LAK, ALG, CAR), relative humidity was downloaded from the site <http://www.wunderground.com>. As oil accumulates in the mesocarp of olives in roughly 20 weeks (24), we used climatic data from August to December. Latitude, longitude, distance from the sea, and altitude were recorded either in the field by GPS or deduced from "Google Earth". The geological classification was deduced from the U.S. Geological Survey map of Europe, the European soil map, and the IGME5000 geological map of Europe (Pawlewicz, M. J.; Steinshouer, D. W.; Gautier, D.L. (2003) Map Showing Geology, Oil and Gas Fields, and Geologic Provinces of Europe including Turkey; Open File Report 97-470I; Central Region Energy Resources Team, U.S. Department of the Interior, U.S. Geological Survey [<http://pubs.usgs.gov/of/1997/ofr-97-470/OF97-470I/index.htm>]; European Soil Database (v 2.0) European Soil Bureau Network and the European Commission, EUR 19945 EN, March 2004 [<http://eusoiils.jrc.it/>]).

Stable Isotope Ratio Analysis. The analysis of stable isotope $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ (D/H) ratios of bulk olive oils was performed in different European laboratories, using a range of isotope ratio mass spectrometers (Delta plus XL, Delta Plus XP, Delta V, Delta S, ThermoFinnigan, Bremen, Germany; Isoprime, AP2003, GV Instruments Ltd., Manchester, U.K.; Optima Micromass) connected to a pyrolyzer (TC/EA, ThermoFinnigan; EuroPyrOH, Eurovector 3000) for $^{18}\text{O}/^{16}\text{O}$ and D/H or an elemental analyzer (Flash EA 1112, 1110, 1108 ThermoFinnigan; Costech ECS4010; NA2100 Proteins, Carlo Erba, Milan, Italy; Vario EL III, Elementar Analysensysteme GmbH, Hanau/Germany) for $^{13}\text{C}/^{12}\text{C}$. The analytical conditions are reported in Camin et al. (5).

The $^{18}\text{O}/^{16}\text{O}$ and D/H ratios of water were measured using isotope ratio mass spectrometers (SIRA II, VG Fisons, Middlewich, U.K.; Thermo Delta V) connected with a water/ CO_2 equilibration system (ISOPREP, VG Fisons) and/or a pyrolyzer (TC/EA ThermoFinnigan).

The isotope ratios were expressed in $\delta\text{‰}$ versus V-PDB (Vienna – Pee Dee Belemnite) for $\delta^{13}\text{C}$ and V-SMOW (Vienna – Standard Mean Ocean Water) for $\delta^{18}\text{O}$ and δD , according to the following formula: $[(R_s - R_{\text{std}})/R_{\text{std}}] \times 1000$, where R_s is the isotope ratio measured for the sample and R_{std} is the isotope ratio of the international standard. The values were calculated against in-house oil standards, which were themselves calibrated against international reference materials: fuel oil NBS-22 (IAEA, <http://curem.iaea.org/catalogue/SI/index.html>) and sugar IAEA-CH-6 (IAEA) for $^{13}\text{C}/^{12}\text{C}$, benzoic acid IAEA-601 (IAEA) and IAEA-CH-6 (IAEA, with $\delta^{18}\text{O} = +36.4\text{‰}$ vs V-SMOW) (25) for $^{18}\text{O}/^{16}\text{O}$ and NBS-22 for D/H.

The standard deviation of repeatability (S_r) for oil was 0.1‰ for $\delta^{13}\text{C}$, 0.4‰ for $\delta^{18}\text{O}$, and 1‰ for δD , whereas that for water was 0.1‰ for $\delta^{18}\text{O}$ and 1‰ for δD . To ascertain the interlaboratory reproducibility, one extra virgin olive oil interlaboratory comparison material (EVOO ICM) and one water ICM sample were used in each laboratory as quality control material. The standard deviation of reproducibility was good for $\delta^{13}\text{C}$ ($S_R = 0.1\text{‰}$), for δD of water and oil ($S_R = 2\text{‰}$), and for $\delta^{18}\text{O}$ of water ($S_R = 0.2\text{‰}$), but not for $\delta^{18}\text{O}$ of oil ($S_R = 2\text{‰}$). The olive oil $\delta^{18}\text{O}$ values were therefore normalized by assigning by agreement a value of +27.0‰ to EVOO ICM. Calculating S_R of normalized $\delta^{18}\text{O}$ values of around 50 olive oils measured in at least two laboratories, we obtained a fair value (0.6‰).

Table 1. Number of Samples and Data of Geographical, Geological, and Climatic Characteristics (T , Temperature; RH, Relative Humidity) of the Provenience Area

site	no. of oils		no. of water	latitude (deg)	longitude (deg)	distance from the sea (km)	altitude (m asl)	geology	2005			2006		
	2005	2006							mean T (°C)	mean RH (%)	precipitation (mm)	mean T (°C)	mean RH (%)	precipitation (mm)
	Trentino, Italy (TRE)	28							28	40	45.9	10.9	129	211
Carpentras, France (CAR)	20	20	40	44.3	5.2	97	384	limestone	13.4	69	265	15.3	67	279
Tuscany, Italy (TOS)	18	21	40	44.0	11.4	83	343	shale/mudstone/clay/loess	14.8	73	617	16.7	68	302
Barcelona, Spain (BAR)	8	2	36	41.7	2.0	35	362	shale/mudstone/clay/loess	13.2	73	405	14.8	75	349
Chalkidiki, Greece (CHA)	20	20	40	40.1	23.9	1	23	acid magmatic	16.2	60	140	16.3	60	206
Sicily, Italy (SIC)	20	20	40	37.8	14.6	32	672	shale/mudstone/clay/loess	12.8	69	218	16.0	68	332
Algarve, Portugal (ALG)	7	7	38	37.2	-7.1	5	27	limestone	18.8	67	270	19.9	72	341
Lakonia, Greece (LAK)	11	17	40	36.6	22.4	1	105	limestone	17.9	59	629	18.0	60	269

Table 2. Limits of Detection

element/ isotope	LOD oil ($\mu\text{g}/\text{kg}$)	LOD water (mg/L)	element/ isotope	LOD oil ($\mu\text{g}/\text{kg}$)	LOD water (mg/L)	element/ isotope	LOD oil ($\mu\text{g}/\text{kg}$)	LOD water (mg/L)
Li/7	0.008	0.0006	Ni/60	1	0.00020	Ba/137	0.12	0.00012
B/11	0.17	0.015	Cu/63	0.10	0.00005	La/139	0.002	0.00005
Na/23	20	0.51	Zn/66	6	0.00005	Ce/140	0.0050	0.00005
Mg/26	4	0.11	Ga/71	0.001	0.00005	Nd/146	0.004	0.00005
Al/27	3	0.0015	Se/78	0.014	0.0082	Sm/147	0.0010	0.00005
K/39	20	0.005	Rb/85	0.001	0.00006	Eu/151	0.0002	0.00005
Ca/40	25	0.02	Sr/88	0.3	0.0025	Yb/171	0.0004	0.00005
V/51	0.007	0.00036	Mo/98	0.050	0.0002	Lu/175	0.02	0.00005
Mn/56	0.2	0.0002	Cd/111	0.005	0.00005	Tl/205	0.0040	0.00005
Co/59	0.002	0.00006	Cs/133	0.001	0.00005	Pb/206 + 207 + 208	0.1	0.00005
						U/238	0.001	0.00006

Table 3. Mean and Standard Deviation (SD) of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and δD of European Olive Oils and Surface Waters^a

year			TRE	CAR	TOS	BAR	CHA	SIC	ALG	LAK
Oils										
2005	$\delta^{13}\text{C}$ ‰ vs V-PDB	mean	-31.0 d	-29.4 b	-30.2 c	-29.3 bc	-29.3 b	-29.1 ab	-28.6 ab	-28.4 a
		SD	0.4	0.2	0.3	0.2	0.6	0.5	0.3	0.6
	$\delta^{18}\text{O}$ ‰ vs V-SMOW	mean	20.2 e	24.8 b	21.9 d	23.4 c	23.4 c	24.8 b	27.1 a	25.1 b
		SD	0.4	0.5	0.5	0.6	0.6	0.6	0.8	0.7
	δD ‰ vs V-SMOW	mean	-159 e	-150 bc	-154 dce	-151 bcd	-157 de	-146 ab	-139 a	-142 a
		SD	3	2	2	4	5	5	2	5
2006	$\delta^{13}\text{C}$ ‰ vs V-PDB	mean	-30.8 e	-29.1 bc	-30.1 d	-29.3	-29.4 c	-28.6 ab	-28.5 ab	-28.3 a
		SD	0.5	0.5	0.3	0.2	0.2	0.2	0.3	0.4
	$\delta^{18}\text{O}$ ‰ vs V-SMOW	mean	21.6 d	25.5 b	22.3 d	24.5	23.5 c	26.6 a	27.1 a	24.1 c
		SD	0.4	1.4	0.8	1.5	0.3	0.3	0.5	0.3
	δD ‰ vs V-SMOW	mean	-156 c	-149 b	-148 b	-144	-160 c	-141 a	-145 ab	-144 ab
		SD	3	8	3	3	2	2	2	3
2005 + 2006	$\delta^{13}\text{C}$ ‰ vs V-PDB	mean	-30.9 f	-29.3 d	-30.1 e	-29.4 cd	-29.4 d	-28.9 bc	-28.6 ab	-28.4 a
		SD	0.5	0.4	0.3	0.2	0.4	0.4	0.3	0.5
	$\delta^{18}\text{O}$ ‰ vs V-SMOW	mean	20.9 f	25.1 bc	22.1 e	23.6 cde	23.5 d	25.7 b	27.1 a	24.5 c
		SD	0.8	1.1	0.7	0.8	0.5	1.0	0.6	0.7
	δD ‰ vs V-SMOW	mean	-157 cd	-150 b	-151 b	-150 abc	-158 d	-144 a	-142 a	-143 a
		SD	3	6	4	5	5	4	4	4
Waters										
	$\delta^{18}\text{O}$ ‰ vs V-SMOW	mean	-9.9 d	-7.2 c	-6.6 bc	-6.6 bc	-7.3 c	-6.3 b	-3.4 a	-6.3 b
		SD	0.4	0.4	1.6	0.6	0.8	0.8	0.9	0.9
	δD ‰ vs V-SMOW	mean	-65 e	-48 d	-44 cd	-41 c	-43 cd	-40 c	-19 a	-31 b
		SD	2	3	6	5	7	5	5	7

^a The two oils from 2006 Barcelona and the "evaporated" surface waters were not considered in the statistical test (see the text). The significance of HSD for unequal *N* Tukey is reported: groups of one row with different letters are statistically different ($p < 0.001$).

Elemental Analysis. The analyses were performed using an Agilent 7500ce ICP-MS (Agilent Technologies, Tokyo, Japan) equipped with an ASX-520 autosampler (Cetac Technologies Inc., Omaha, NE). An octopole reaction system (ORS) was used to remove polyatomic interferences, using He and H₂ as collision and reaction gas, respectively.

The samples were prepared and analyzed according to the method of Camin et al. (5), with minor modifications. The extracting water solution was prepared with 6.7% H₂O₂ (30% Superpure, Merck, Darmstadt, Germany), 1% HNO₃ (Superpure, Merck), and 0.2% HCl (ACS; Riedel-deHaën, Seelze, Germany). All of the materials were washed with 5% HNO₃ and rinsed with Milli-Q water before use. Sample preparation and analysis were carried out in triplicate. The limit of detection (LOD) of each element was calculated as 3 times the standard deviation of the signal of the blank samples, extracted and analyzed 10 times (Table 2).

Because an international vegetable oil is not available, accuracy was checked by using two spiked samples in each analytical run. The first spiked sample was prepared by adding one defined aliquot (around 0.5–1 g) of the standard reference material NIST 2387 (semisolid

peanut butter) to 15 g of a natural olive oil and mixed thoroughly. The second sample was obtained by spiking 15 g of olive oil with 40 mg of SPEX s-23 100z (organometallic multistandard certified mineral oil). The natural oil and the fortified mixtures were extracted and analyzed three times. Recovery was calculated on the difference of the mean content of the spiked and the unspiked samples. Using the NIST standard, the recoveries for the six elements were 82% for Zn, 84% for Mn, 90% for Ca, 92% for Mg, 95% for K, and 101% for Na, whereas those obtained using the SPEX standard for the 15 elements were lower (B, 88%; Na, 80%; Mg, 67%; Al, 53%; K, 92%; Ca, 84%; V, 63%; Mn, 71%; Ni, 65%; Cu, 61%; Zn, 68%; Mo, 66%; Cd, 71%; Ba, 65%; Pb, 67%), perhaps as a consequence of the difficulty of obtaining a well-homogenized spiked sample.

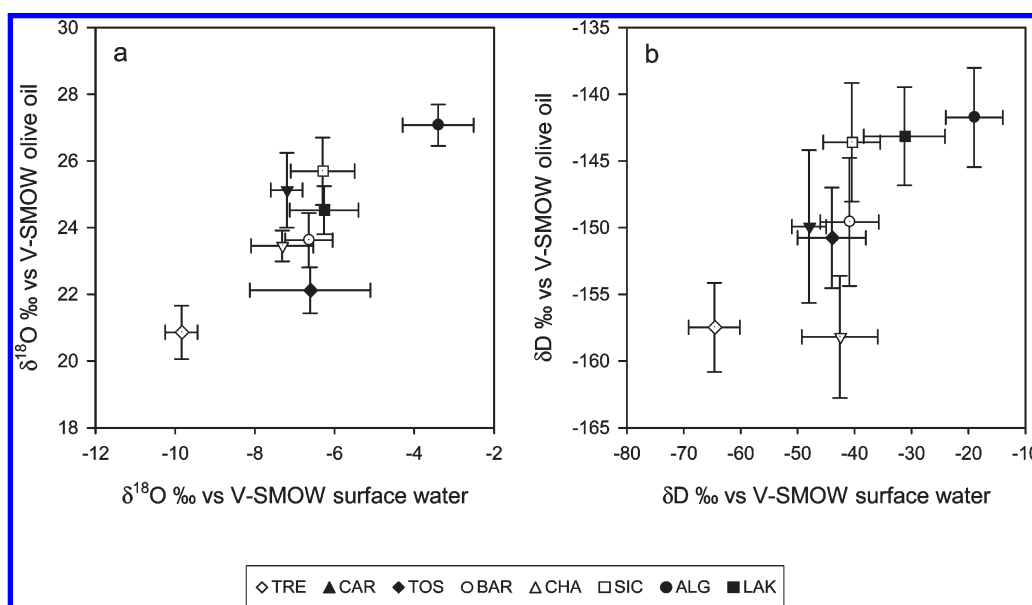
The precision (RSD%) of the analytical method, evaluated by preparing and analyzing an oil sample 10 times, ranged from 13 to 27% for the different elements. These values can be deemed satisfactory, considering the very low content of elements in olive oil.

Statistical Analysis. The data were statistically evaluated using Statistica v 8 (StatSoft Italia srl, Padua, Italy).

Table 4. Pearson Coefficient, Significance and Regression Coefficient (Intercept and Slope) of the Correlation between Isotopic Values and Geographical and Climatic Factors^a

		$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	δD	latitude (DD)	longitude (DD)	distance from the coast (km)	altitude (m asl)	temp ($^{\circ}\text{C}$)	relative humidity	rain (mm)
Olive Oil											
$\delta^{13}\text{C}$	<i>r</i>		0.82	0.62	-0.80	0.13	-0.75	0.07	0.59	-0.61	-0.29
	<i>r</i> ²		0.67	0.38	0.64	0.02	0.56	5×10^{-3}	0.35	0.38	0.09
	signif		<0.001	<0.001	<0.001	0.0377	<0.001	0.2687	<0.001	<0.001	<0.001
	intercept		-38.30	-17.67	-20.46	-29.75	-28.71	-29.63	-33.70	-22.20	-28.85
	slope		0.370	0.079	-0.218	0.015	-0.014	3×10^{-4}	0.273	-0.108	-0.002
$\delta^{18}\text{O}$	<i>r</i>	0.82		0.70	-0.67	-0.16	-0.58	0.21	0.51	-0.41	-0.32
	<i>r</i> ²	0.67		0.49	0.45	0.03	0.34	0.04	0.26	0.17	0.10
	signif	<0.001		<0.001	<0.001	0.0076	<0.001	0.001	<0.001	<0.001	<0.001
	intercept	76.69		53.38	40.50	24.13	25.05	23.09	15.84	34.41	25.31
	slope	1.796		0.197	-0.405	-0.042	-0.024	0.002	0.512	-0.159	-0.005
δD	<i>r</i>	0.62	0.70		-0.56	-0.19	-0.37	0.27	0.43	-0.17	0.003
	<i>r</i> ²	0.38	0.49		0.31	0.03	0.13	0.08	0.18	0.03	1×10^{-5}
	signif	<0.001	<0.001		<0.001	0.0023	<0.001	<0.001	<0.001	0.0047	0.9548
	intercept	-8.80	-209.38		-100.93	-148.63	-147.53	-153.20	-173.96	-134.61	-150.84
	slope	4.803	2.483		-1.196	-0.171	-0.054	0.009	1.530	-0.238	2×10^{-4}
Water											
$\delta^{18}\text{O}$	<i>r</i>			0.93	-0.62	-0.26	-0.55	-0.47	0.54	-0.30	-0.01
	<i>r</i> ²			0.87	0.39	0.07	0.390	0.22	0.29	0.09	0.0002
	signif			<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.8297
	intercept			-1.60	6.19	-6.35	-5.94	-5.96	-12.93	-1.15	-6.86
	slope			0.125	-0.319	-0.047	-0.022	-0.003	0.409	-0.085	-0.0001
δD	<i>r</i>		0.93		-0.76	-0.07	-0.72	-0.54	0.70	-0.51	0.05
	<i>r</i> ²		0.87		0.58	0.01	0.52	0.29	0.49	0.26	0.002
	signif		<0.001		<0.001	0.22	<0.001	<0.001	<0.001	<0.001	0.4292
	intercept		5.62		77.78	-41.40	-33.10	-34.37	-101.25	32.07	-43.91
	slope		6.982		-2.938	-0.102	-0.216	-0.023	3.984	-1.102	0.004

^aNumbers given in boldface are evidence of the nonsignificant correlation ($p \geq 0.001$). DD, decimal degrees.

**Figure 1.** Plot of the mean values and the respective standard deviations of $\delta^{18}\text{O}$ (a) and δD (b) values of olive oil against those of water.

RESULTS AND DISCUSSION

Stable Isotope Ratios. In Table 3 the mean and standard deviation of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and δD values of olive oils, grouped according to origin and production year and ordered in inverse proportion to

latitude, are shown. By applying the Kolmogorov–Smirnov test (26), the isotopic data was normally distributed into the groups.

The isotopic parameters were significantly ($p < 0.001$, Person's correlation test) correlated with each other (Table 4). The linear

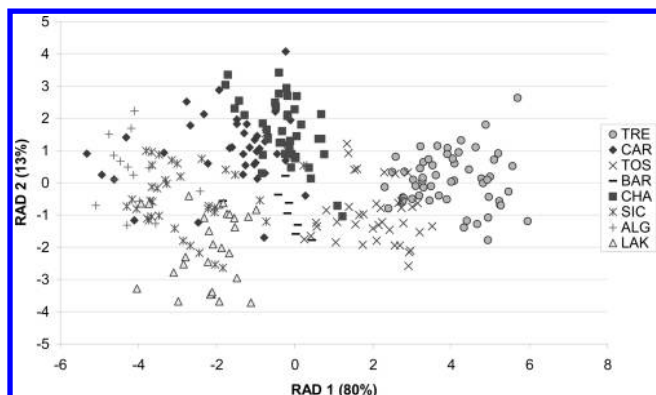


Figure 2. Canonical discriminant analysis of $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ of the olive oils from the eight European sites: scatterplot of the first two canonical variables.

Table 5. Reclassification Discriminant Analysis of $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ of the Olive Oils from the Eight European Sites: Results of Classification Matrix

	% correctly classified	TRE	CAR	TOS	BAR	CHA	SIC	ALG	LAK
TRE	91	51	0	5	0	0	0	0	0
CAR	70	0	28	1	0	3	4	4	0
TOS	87	5	0	34	0	0	0	0	0
BAR	40	0	1	1	4	3	1	0	0
CHA	90	0	1	3	0	36	0	0	0
SIC	63	0	8	0	2	0	25	3	2
ALG	57	0	0	0	0	0	6	8	0
LAK	79	0	0	0	0	0	6	0	22

equation of δD versus $\delta^{18}\text{O}$ values ($\delta\text{D} = 2.48 \times \delta^{18}\text{O} - 209.38$) is similar to the one found for Italian PDO olive oils ($[\delta\text{D} = 2.5091 \times \delta^{18}\text{O} - 208.1, \text{Camin et al. (5)}; \delta\text{D} = 2.663 \times \delta^{18}\text{O} - 210.04, \text{Bontempo et al. (6)}]$). It therefore can be inferred that olive oil δD and $\delta^{18}\text{O}$ values correlate on a worldwide scale, likewise to water [Global Meteoric Water Line (27)].

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ showed significant correlation (Pearson's correlation test, $p \leq 0.001$) to latitude, distance from the coast, temperature, relative humidity, and amount of precipitation of the last 5 months before harvest, even if in some cases with very low r^2 , whereas δD correlates with latitude, distance from the coast, altitude and temperature (Table 4). The deviation of the δD values from the geographical and climatic gradient for Chalkidiki for both years (Table 3) could be justified on the basis of the olive size, because Chalkidiki olives were quite big (3 cm long and 1.5 cm round), for example, in comparison to olives from Lakonia, Carpentras, and Trentino (1–1.5 long and ~0.5 cm round) and therefore could be subjected to different kinetic fractionation during evapotranspiration (28). In contrast to previous studies (6, 7), specific weather stations were considered for each site, and we found more significant correlations with temperature and relative humidity. The slope and intercept of the linear equations of $\delta^{18}\text{O}$ versus latitude, temperature, and humidity are comparable to those of the literature (6, 7).

ANOVA and Honestly Significantly Different (HSD) for unequal N Tukey tests highlight statistically significant ($p < 0.001$) differences in the values of all three isotopic parameters among the olive oils produced in the eight sites (Table 3), both within each year or considering the two years together. The two olive oils from Barcelona were excluded from the statistical evaluation of 2006, because they were not representative from a statistical point of view. Comparing the two years' data, we found differences ($p < 0.001$) between 2005 and 2006 data for $\delta^{18}\text{O}$ in

TRE, SIC, and LAK and for δD in TRE, SIC, TOS, and ALG. The different climatic conditions of the last 5 months (period of oil accumulation, see Table 1) between the two years can justify these differences (6).

Considering the two years together, $\delta^{13}\text{C}$ allows to discriminate ($p < 0.001$) TRE; TOS; the group CAR, BAR, CHA; the group ALG, LAK; most of all along a latitudinal gradient, except for TOS and CAR, for which the climatic conditions play a significant role. The $\delta^{18}\text{O}$ improves the discrimination between ALG and LAK and together with δD between CAR and CHA.

Similarly to olive oils, the $\delta^{18}\text{O}$ and δD values of the surface waters (Table 3) collected from the same sites were significantly affected by the site (ANOVA test) and correlated (Pearson's test, $p \leq 0.001$) with temperature, relative humidity, latitude, distance from the sea, and altitude (Table 4), in some cases with very low r^2 . Of the 314 water samples, we do not consider 20 from ALG, 11 from TOS, and 4 from each CAR, TRE, and SIC, because the d -excess value $> 2\%$ indicated high water evaporation (29).

As expected, $\delta^{18}\text{O}$ and δD values of surface waters correlated with each other: most of the samples were along the Global Meteoric Water Line (GMWL; $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$), whereas Lakonia and Chalkidiki along the Mediterranean water line ($\delta\text{D} = 8 \times \delta^{18}\text{O} + 20$) (30).

In comparison to water, olive oils are enriched in ^{18}O to around 30‰ and depleted in D to about 120‰, as a consequence of the fractionation occurring in plants during the photosynthesis and biosynthetic pathways of lipids (18, 19).

The parametric HSD for unequal N Tukey test applied to the water samples recognizes fewer groupings for $\delta^{18}\text{O}$ with respect to the olive oils and less deviation for both elements to the climatic and geographical (latitude, distance from the sea) gradient. By plotting the mean values of olive oil against those of water (Figure 1), a relationship between the isotopic composition of olive oils and that of the local water is evident, even if not unequivocal, due to the effect of climatic and physiological factors on evapotranspiration processes in plants.

To assess the discrimination efficiency for olive oil origin, a multivariate analysis of the two years' data was carried out by discriminant analysis (using standard procedure), which maximized the differences between the groups by means of a linear combination of the variables (31). By applying canonical discriminant analysis, three different independent discriminant functions (RAD) were computed. The combination of the first two canonical variables RAD1 (80%) and RAD2 (13%) accounted for 93% of variability (scores plot shown in Figure 2). RAD1 is loaded negatively with $\delta^{18}\text{O}$ (standardized coefficient, -0.72) and $\delta^{13}\text{C}$ (-0.52), whereas RAD2 is mainly determined negatively by $\delta^2\text{H}$ (-1.08) and positively by $\delta^{18}\text{O}$ (0.80). Some geographical groupings are evident, as confirmed by applying the reclassification discriminant analysis, where 77.9% of the 267 samples were correctly reclassified (Table 5).

Elemental Composition. Of the 31 analyzed elements, Ca was present in detectable amounts in 98% of samples, Rb in 92%, K and Mg in 88%, Cu in 82%, Zn in 67%, U in 61%, La in 57%, Mn in 55%, Ba in 53%, Ce in 53%, Cs in 51%, Na in 50%, Pb in 49%, B in 44%, Sm in 39%, Co in 38%, Yb in 36%, Nd in 35%, Eu in 34%, Sr in 32%, Li and V in 31%, Ga in 21%, Al in 19%, Ni in 10%, Cd in 7%, Tl in 4%, Se in 3%, and Mo and Lu in 1% of the samples.

Table 6 shows the median contents quantified for each element in the 267 olive oil samples for each site and for the 3 geological classes, as well as the median content in the 313 surface waters for the 3 geological classes (1 water from BAR was not measured). Median values were displayed because of the non-normal

Table 6. Median Values of Elements of European Olive Oils and Results for Geological Origin of HSD for Unequal N Tukey Test ($p < 0.05$) Applied on Normalized and Box-Cox Transformed Data

element	olive oils ($\mu\text{g/kg}$)										surface waters (mg/L)											
	shale/clay/mudstone/loess					limestone					acid magmatic			shale/clay/mudstone/loess			limestone			acid magmatic		
	SIC	TOS	BAR	median	signif	TRE	LAK	ALG	CAR	median	signif	CHA	signif	median	signif	median	signif	median	signif	median	signif	median
Li	0.009	<0.008	0.016	<0.008	<0.008	<0.008	<0.008	0.018	0.068	<0.008	<0.008	<0.008	0.00706	a	0.00128	b	0.00526	a				
B	<0.17	<0.17	0.40	<0.17	0.81 <0	<0.17	0.19	0.81	<0.17	<0.17	<0.17	<0.17	0.0525	a	0.0240	b	0.0174	b				
Na	36	34	22	31	<20	<20	65	231	34	34	<20	<20	22.10	b	11.41	c	51.49	a				
Mg	12	15	14	15	9	28	97	58	19	19	13	ab	14.07	a	8.09	b	17.06	a				
Al	<3	<3	<3	<3	<3	<3	<3	5	<3	<3	<3	ab	0.0028	b	<0.0015	b	0.0096	a				
K	184	85	204	156	62	54	403	47	62	62	92	a	2.280	b	1.531	c	2.506	a				
Ca	95	117	73	100	011	144	361	401	133	133	128	a	74.45	a	52.54	b	29.27	c				
V	<0.007	0.016	<0.007	0.009	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	ab	<0.00036	b	<0.00036	b	0.00050	a				
Mn	<0.2	<0.2	1.1	<0.2	<0.2	0.6	3.7	0.7	0.5	0.5	0.6	a	0.000	b	0.015	c	0.0158	a				
Co	<0.002	<0.002	0.02	<0.002	<0.002	<0.002	0.025	0.010	<0.002	<0.002	0.003	a	0.00016	b	0.00014	c	0.00014	a				
Ni	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	ab	0.00089	a	0.00027	b	0.00043	ab				
Cu	0.31	0.35	0.87	0.3	0.33	0.310	1.55	0.36	0.3	0.3	0.51	a	0.00114	a	0.36	b	0.00026	b				
Zn	7	11	7	8	170	12	40	21	12	12	11	a	0.0017	a	0.0017	b	0.0009	a				
Ga	<0.001	<0.001	0.005	<0.001	<0.001	<0.001	0.005	0.001	<0.001	<0.001	<0.001	a	0.00150	a	0.00061	b	0.00150	a				
Se	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	a	<0.0082	b	<0.0082	a	<0.0082	a				
Rb	0.133	0.043	0.157	0.113	0.024	0.031	0.254	0.045	0.039	0.039	0.077	a	0.00056	b	0.00061	a	0.00049	a				
Sr	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	1.2	1.9	<0.3	<0.3	<0.3	b	0.51870	a	0.14988	b	0.30638	b				
Mo	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	a	0.00060	a	0.00024	b	0.00047	a				
Cd	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.007	<0.005	<0.005	<0.005	<0.005	a	<0.00005	b	<0.00005	a	<0.00005	a				
Cs	<0.001	<0.001	0.01	<0.001	0.006	<0.001	0.043	0.011	0.006	0.006	<0.001	ab	<0.00005	b	<0.00005	a	<0.00005	a				
Ba	<0.12	0.13	0.18	<0.12	0.360	<0.12	0.33	0.57	0.36	0.36	0.37	a	0.06	a	0.01811	b	0.03912	ab				
La	<0.0020	<0.0020	0.0375	<0.0020	<0.0020	0.0046	0.0296	0.0194	0.0052	0.0052	0.0037	a	<0.00005	c	<0.00005	b	0.00015	a				
Ce	<0.0050	0.0083	0.0522	<0.0050	<0.0050	0.05050	0.0505	0.05	0.0081	0.0081	<0.0050	ab	<0.00005	c	<0.00005	b	0.00018	a				
Nd	<0.004	<0.004	0.018	<0.004	<0.004	0.005	0.025	0.00	0.005	0.005	<0.004	a	<0.00005	c	<0.00005	b	0.00013	a				
Sm	<0.0010	<0.0010	0.0072	<0.0010	<0.0010	<0.0010	0.0078	0.0048	0.0015	0.0015	<0.0010	ab	<0.00005	c	<0.00005	b	<0.00005	a				
Eu	<0.0002	<0.0002	0.0051	<0.0002	<0.0002	<0.0002	0.0052	0.0049	0.0003	0.0003	<0.0002	ab	<0.00005	b	<0.00005	a	<0.00005	a				
Yb	<0.0004	<0.0004	0.0046	<0.0004	<0.0004	<0.0004	0.0047	0.0050	0.0005	0.0005	<0.0004	a	<0.00005	b	<0.00005	a	<0.00005	a				
Lu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	a	<0.00005	b	<0.00005	a	<0.00005	a				
Tl	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	a	<0.00005	b	<0.00005	a	<0.00005	a				
Pb	<0.1	<0.1	0.5	<0.1	<0.1	<0.1	1.5	0.6	0.1	0.1	<0.1	a	<0.115	b	<0.115	a	<0.00005	a				
U	<0.001	<0.001	0.046	<0.001	0.003	0.021	0.0	0.0	0.005	0.005	0.018	a	0.00071	b	0.00025	c	0.00061	a				

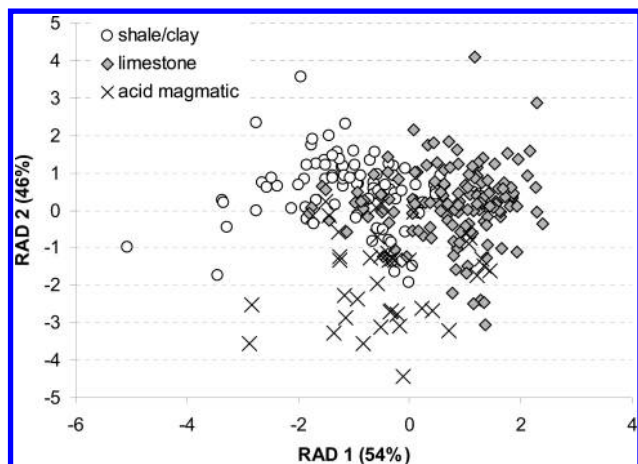


Figure 3. Canonical discriminant analysis of the elemental content of the olive oils from three geological origins: scatterplot of the first two canonical variables.

distribution of the raw data (Kolmogorov–Smirnov and Shapiro–Wilk tests).

For the statistical elaboration we considered all of the raw data, also including the values lower than the detection limit. For every sample, the content of each element was normalized by dividing it by the sum of the content of all the elements. This was done to minimize possible problems due to salt crystallization in organic matrix and settling.

After the Box–Cox transformation, a normal distribution of data was obtained for each element, with the exception of Li.

ANOVA and HSD for unequal *N* Tukey tests, performed on Box–Cox-transformed data, highlight statistically significant ($p < 0.05$) differences in the content of 16 elements (Mg, Al, K, Ca, V, Mn, Ni, Zn, Rb, Sr, Ce, Sm, Cs, La, Eu, U) among the olive oils produced in the 3 different geological zones (Table 6). Al and Ni were excluded from the multivariate statistical elaboration as they were quantifiable (amount > LOD) in < 30% of samples.

The canonical multivariate discriminant (standard) analysis performed on olive oils using the 14 elements produced 2 canonical variables (RAD 1 and RAD 2) explaining 54 and 46% of variability, respectively (Figure 3). The elements with higher standardized coefficients were Cs (0.88), V (−0.82), and Rb (−0.81) for RAD 1 and Sm (−0.67), Ce (0.59), U (−0.73), Ca (−0.70), and Rb (−0.63) for RAD 2.

Overall, 76% of the samples were correctly classified into the 3 geological typologies: 83% of limestone samples, 63% of acid magmatic samples, and 72% of clay/shale samples were classified correctly; 17 oil samples collected on a limestone geology were erroneously classified as belonging to a clay/shale zone and 6 to a magmatic zone, and 9 and 6 samples collected on an acid magmatic geology were misclassified as belonging to a limestone and clay/shale zone, respectively, whereas 20 samples obtained in a clay/shale zone were assigned to a limestone zone and 5 to an acid magmatic zone.

Of the 14 discriminant elements for oils, 10 also proved to be significant (ANOVA, $p < 0.05$) for surface water differentiation, although the median values of the three geological types were not always in the same order in olive oils and waters. This could be due to possible physiological effects such as root absorption or plant translocation/accumulation or to the different solubilities of the elements in water and oils.

By applying multivariate discriminant analysis on the 14 elements, 82% of the 313 surface water samples were correctly classified into the 3 geological groups (the elemental profile of

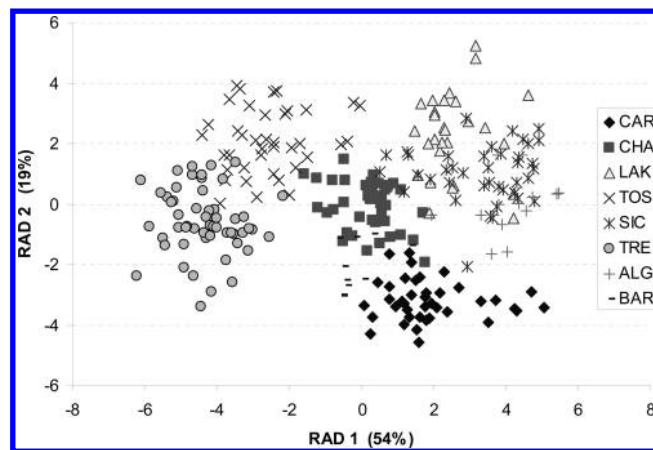


Figure 4. Canonical discriminant analysis of the isotopic and elemental composition of the olive oils from the eight European sites: scatterplot of the first two canonical variables.

Table 7. Reclassification Discriminant Analysis of the H, C, and O Stable Isotope Ratios and Elemental Composition of the Olive Oils from the Eight European Sites: Results of Classification Matrix

	% correctly classified	TRE	CAR	TOS	BAR	CHA	SIC	ALG	LAK
TRE	95	53	0	2	0	1	0	0	0
CAR	98	0	39	0	1	0	0	0	0
TOS	97	1	0	38	0	0	0	0	0
BAR	100	0	0	0	10	0	0	0	0
CHA	98	0	0	1	0	39	0	0	0
SIC	95	0	0	0	0	0	38	0	2
ALG	100	0	0	0	0	0	0	14	0
LAK	86	0	0	0	0	0	3	1	24

1 water from BAR is missing). Twenty-two of 115 water samples collected on clay/shale geology were erroneously classified as belonging to a limestone zone, whereas 27 of 158 samples collected in a limestone zone and 5 of 40 collected in an acid magmatic zone were assigned to a clay/shale geology. Two samples collected on a limestone geology were classified as belonging to a magmatic zone, and 1 sample belonging to the acid magmatic geology was assigned to a limestone zone.

The selected 14 elements seem to be a good starting point to geologically characterize the origin of olive oils, as well as surface water.

Geographical Discrimination of Olive Oils Using Isotopic and Elemental Analysis. By combining the 3 isotopic ratios and the 14 elements described above, an improved separation of samples produced at the 8 sites is obtained (Figure 4). Using standard and forward stepwise discriminant analysis, which kept all 14 selected trace elements and the 3 isotopic ratios in the model, 7 canonical variables were identified. The first and second variables account for 73% of the variability (54 and 19%, respectively). The higher standardized coefficients were obtained for $\delta^{18}\text{O}$ (0.74), $\delta^{13}\text{C}$ (0.58), La (0.56), and Ce (−0.83) for RAD 1 and for U (0.81), Ce (0.87), Ca (0.65), V (0.60), La (−1.02), and Sr (−0.58) for RAD 2. RAD3 (12%), loaded mainly by K (0.82), Ca (0.81), U (0.52), δD (−0.75), and Sm (−0.50), improves the separation between Lakonia and Sicily.

A total of 95.5% of the olive oil samples could be correctly classified to the production site (Table 7).

To test the predictive discrimination power and the stability of the model, some of the analyzed samples were used as unknowns to validate the model built on the basis of the remaining cases. In detail, 3 different sets of 26 olive oils (10% of the original database; 4 SIC, 4 TOS, 4 CAR, 4 CHA, 5 TRE, 3 LAK,

1 BAR, 1 ALG randomly selected) were removed from the data, and each time the model was calculated on the remaining 241 cases and was validated with all 267 samples (including the excluded oils). In all analyses, around 95% (from 95.1 to 95.5%) of the samples were correctly classified.

The reclassification of the unknown samples indicates the stability of the model.

To use the model for verifying claim of origin of commercial olive oils, a larger number of authentic samples must be analyzed, considering also other European production sites, as has been done since 1987 for wine (EU Regulation 555/2008).

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