



Article

Screening of the Volatile Composition of Moroccan Olive Oils by Using SPME/GC-MS-FID over a Two-Year Period: A Pedoclimatic Discrimination

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Abstract: The volatile profile of an olive oil is a crucial attribute indicating its sensory quality. Hence, to elucidate the impact of geographical origin (including edaphoclimatic conditions) and the crop season on the volatile composition of monovarietal Moroccan olive oil “Picholine Marocaine”, over a two-year harvest period (2018/19 and 2019/20), thirty-eight olive oil samples were obtained from nineteen Moroccan areas well-known by the abundance of olive tree cultivation. By using SPME/GC-FID-MS, 229 and 215 volatile compounds were characterized in olive oils produced during the 2018/19 and 2019/20 crop years, respectively. The identified compounds belong to nine volatile groups: terpenes, hydrocarbons, furans, esters, alcohols, acids, ketones, aldehydes, and nitrogen compounds. The one-way ANOVA and interactive heatmap revealed significant differences in the volatiles proportion in oils from different geographical origins. Our results imply that environmental (edaphoclimatic) conditions considerably influence the volatile compounds’ biosynthesis, e.g., when soil granulometry decreases (from sand to silt), alcohols become esters due to the activity of alcohol dehydrogenase (ADH) and alcohol acetyl transferase (AAT) enzymes. Moreover, our findings exhibit a significant influence of the crop season on the volatile composition of Moroccan olive oils.

Keywords: volatile fraction; olive oil; Picholine Marocaine; GC-MS/GC-FID; linear retention index (LRI); pedo-climate; crop year



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1. Introduction

Olive oil (*Olea europaea* L.) is a staple food in the Mediterranean countries and the most appreciated edible oil all over the world due to the presence of monounsaturated fatty acid (mainly oleic acid) and the minor compounds (phenolic and aromatic fractions) that supply olive oil with its high nutritional value [1]. At present, because of the considerable nutritional and economic virtues, olive oil’s quality is considered a vital element in competitiveness [2]. According to the data reported by the International Olive Council (IOC) [3], the global production and consumption of this prestigious oil have increased from 1.45 to 3.62 and from 1.66 to 3.05 million tons, respectively, in the last two decades (1990/91–2018/19).

The fragrant and pungent flavor of olive oil turned in a considerable expansion of this valuable food in non-Mediterranean countries too; hence, it is of great popularity

among other edible oils because of this pleasant flavor, aroma, and color that are the main sensations contributing to the acceptability of foodstuffs by consumers [4–6]. As the overall food's quality is impacted by its flavor [7], particular research attention has been given to identifying the compounds contributing to the peculiar flavor of olive oil [8]. It was noticed that these sensory attributes are principally ascribable to the concentration and nature of volatile compounds (VCs) that mainly develop during and after oil's extraction [6], and somehow to some phenolic compounds [1,9,10]. In detail, the VCs and non-VCs (i.e., phenolic fractions) stimulate olfactory and tasting receptors, respectively [11].

The volatile fraction is a class of compounds with a low molecular weight (less than 300 Da) and high vapor pressure at room temperature. They are formed by cell destruction, so an enzymatic process involves hydrolysis and oxidation that proceed at a high rate depending on the pH and temperature [12]. In olive oils, many volatiles originated from the enzymatic pathways inside olives during extraction [10], mainly produced by the oxidation of fatty acids [1]. Furthermore, the volatile fraction is strongly related to the desirable and undesirable odor attributes of VOOs [13,14], which are formed differently: positive aroma perceptions are originated from biogenic pathways (endogenous enzymes) by the autoxidation of unsaturated fatty acid through lipoxygenase pathways (LOXs) [15,16]; however, the sensory defects (off-flavors), e.g., rancid, winey–vinegary, fusty notes are generally produced by chemical oxidation and exogenous enzymes [1,4].

In recent decades, a high number of olive oil's volatile compounds were identified in several countries. Some precedent research revealed approximately 280 volatile compounds, of which, 67 contribute to the aroma and 20 to the sensory defects in VOOs [17]. Moreover, according to Genovese et al. [9], about 180 aromatic compounds, including aldehydes, alcohols, esters, hydrocarbons, ketones, furans, and terpenes, were identified, to date, in VOOs. In fact, at present, many authors, e.g., [4,6,18–20], have provided lists of the identified volatiles in olive oil while classifying them according to their functional groups: aldehydes, alcohols, esters, hydrocarbons, phenols, ketones, sulfur compounds, furans, ethers, organic acids, and terpenes.

Bearing in mind, volatiles (particularly hydrocarbons [20,21]) are relevant geographical and varietal markers to distinguish VOOs in traceability studies [22,23] as they are used for the characterization of monovarietal VOOs [6]. Nevertheless, the profile of this fraction in olive oil is affected by several internal and external factors [24,25], including the geographical origins, i.e., latitude and longitude [26], pedoclimatic conditions [27,28]; soil [29] and climate [26], tree age [30], the variety [31], the growing practice such as the irrigation regime [32,33], harvest time [34], processing method [16] such as malaxation time, temperature and the mill types [31,35], as well as the storage conditions and packaging material [36].

Despite the increasing concern over olive oil quality globally, the research to date has tended to focus on olive oil profiles (in terms of bioactive fraction, fatty acids, or volatile compounds) and on the geographical discrimination rather than the impact of soil and climate (except [26–29]). Thus, the influence of pedoclimatic conditions on volatile compounds is not yet clear. Indeed, the research presented herein is a complementary study of our precedent works on the phenolic fraction [37] and fatty acids [38] composition in Moroccan olive oils from the well-producing olive areas. It was designed to firstly assess the sensory profile of thirty-eight monovarietal Moroccan olive oils (“Picholine Marocaine”) over two successive crop seasons (2018/19 and 2019/20), and secondly, to investigate their association with the geographical origins, including soil and climate conditions. On the other hand, as the SPME-GC/MS is a sophisticated technique used for olive oil authentication, including volatile compound analysis [13], all samples were analyzed by using headspace solid-phase microextraction coupled to gas chromatography with flame ionization and mass spectrometry detectors (SPME/GC-FID-MS).

2. Materials and Methods

2.1. Olive Oil and Soil Samples

Thirty-eight monovarietal olive oil samples (“Picholine Marocaine”) were collected from nineteen Moroccan mills during the 2018/19 and 2019/20 crop years. Before the analysis, all the sampled oils were transported and stored in brown, glass bottles at 4 °C in dark containers. With regard to soils, samples were taken at 0–60 cm depths from the same olive oil production areas while using an Edelman’s Auger.

2.2. The Study Area

The present work was conducted in the central producing regions of olive oils in Morocco. The choice of the study zone was based on an in-depth study of the olive oil-producing regions in Morocco, mainly the regional distribution and the abundance of olive trees, climate, and high olive oil production. The nineteen chosen sampling areas belong to five administrative regions (Tangier-Tetouan-Al Hoceïma, Rabat-Sale-Kenitra, Fes-Meknes, Beni Mellal-Khenifra, and Marrakech-Safi). In detail, the study zone was located as follows: 4°20′58″–9°31′21″ °W (longitude), 35°2′51″–31°34′58″ °N (latitude), and between 40.65 and 947.11 m of height. The geographical coordinates (latitude, longitude, and altitude) were collected while using Merchich North Morocco’s coordinate system. In addition, the rainfall (mm) data were provided from <http://chrsdata.eng.uci.edu/> (accessed on 7 September 2020); however, temperature (°C), relative humidity (%), and wind speed (m/s) were collected from <https://power.larc.nasa.gov/> (accessed on 22 September 2020).

2.3. Chemical and Reagents

A C7–C40 saturated alkanes (1000 µg/mL) standard mixture in hexane supplied by Merck Life Science (Merck KGaA, Darmstadt, Germany) was used for ALKANEs linear retention index (LRI) calculation. Before the analysis, all the standards were maintained at –20 °C.

2.4. Sample Preparation

Volatile compound extraction was performed for 50 min at 60 °C by adding a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm fiber 1 cm long into a 10 mL SPME vial containing 1 mL of extra virgin olive oil.

2.5. SPME-Extraction Conditions

For the method optimization, carboxen/polydimethylsiloxane (CAR/PDMS) 75 µm fiber 1 cm long and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm fiber 1 cm long were tested. Both fibers were purchased by Merck Life Science (Darmstadt, Germany) and were conditioned before the initial use according to the manufacturer’s instructions. A cleaning step of 20 min at 10 °C below the fiber’s recommended maximum temperature was applied between consecutive analyses. Sample conditioning times of 5 and 10 min were evaluated at the same temperature for the extraction stage, and the analytical repeatability was excellent in both conditions. Different stirring rates (200 and 300 rpm) were also investigated. Different volumes of sample were also tested: 1.0, 2.0, and 3.0 mL and the best results were obtained for with a 1.0 mL sample volume in a 10 mL SPME vial. Three different fiber exposure times were also tested: 30, 40, and 50 min. The highest volatile extraction yield was achieved following an exposure time of 50 min, by using a (DVB/CAR/PDMS) 50/30 µm fiber a conditioning time of 5 min, and an extraction temperature of 60 °C, and a stirring rate of 300 rpm. Following the extraction, the analytes were thermally desorbed for 1 min at 260 °C in the GC injector port in splitless mode.

2.6. GC-MS and GC-FID Analyses

GC-MS analyses were conducted on a GCMS-QP2020 instrument (Shimadzu, Kyoto, Japan). For the separation, an SLB-5 ms fused-silica capillary column of 30 m × 0.25 mm i.d. × 0.25 µm df (Merck Life Science, Merck KGaA, Darmstadt, Germany) was applied.

Helium was used as a carrier gas at a constant linear velocity of 30.0 cm/s, corresponding to an inlet pressure of 24.2 kPa. The temperature program was the following: 40 °C held for 1 min to 350 °C at 3 °C/min, held for 5 min. The interface and ion source temperatures were 250 °C and 200 °C, respectively. The acquisition was performed in full-scan mode in the mass range of 40–500 m/z, with a scanning rate interval of 0.2 s. Data handling was supported by GCMS solution ver. 4.30 software (Shimadzu, Kyoto, Japan). For the characterization, the following databases were used: W11N17 (Wiley11-Nist17, Wiley, Hoboken, USA; and FFNSC 4.0 (Shimadzu, Kyoto, Japan). The identification was performed by applying two filters: a spectral similarity match over 85% and linear retention index (LRI) match with a filter window of ± 10 LRI units.

GC-FID analyses were performed on a GC-2010 instrument (Shimadzu, Kyoto, Japan). The oven-temperature program and injection parameters were the same as for MS applications. Helium was used as a carrier gas at a constant linear velocity of 30.0 cm/s, corresponding to an inlet pressure of 97.4 kPa. The injector temperature was set at 260 °C. The FID temperature was set at 280 °C (sampling rate 200 ms); hydrogen and air flow were 40 mL/min and 400 mL/min, respectively. The data were collected by LabSolution software ver. 5.92 (Shimadzu, Kyoto, Japan). Quantitative results were determined as peak area percentage without any corrections. The samples were analyzed in triplicates.

2.7. Soil Analysis

Once in the laboratory, the sampled soils were immediately subjected to drying, crushing, and sieving manually with 0.2 mm and 2 mm mesh screens. Subsequently, the measurements of nine soil variables, viz., soil texture (silt, clay, and sand), pH, conductivity, carbon and organic matter, limestone, NPK (nitrogen, phosphorus, and potassium) nutrients, and exchangeable cations (Ca^{2+} , Mg^{2+} , K^{+} , Na^{+}), were performed in duplicate, as described in our previous papers [37,38].

2.8. Statistical Analysis

The results of the GC-MS and GC-FID analyses were expressed in area % as the mean value and standard deviation of three replicates (mean $\pm$ SD). Comparisons between the detected volatile classes in olive oils obtained from different geographical origins were conducted by applying one-way ANOVA with Tukey's HSD post hoc test, and the significance was fixed at 5% ($p < 0.05$). In the current study, all the statistical tests (viz., one-way ANOVA, correlation analysis, and heatmap) were performed by using R software version 4.1.0. Xtable R and heatmaply packages were used to display the correlation matrix using Pearson's correlation coefficient and the interactive heatmap, respectively.

3. Results and Discussion

3.1. Volatile-Fraction Analysis

The detected volatile compounds in the thirty-eight analyzed monovarietal "Picholine Marocaine" EVOOs are presented in Tables S1 and S2. More than two hundred volatile compounds, i.e., 229 and 215 components, were, respectively, identified in olive oils obtained during the 2018/19 and 2019/20 crop years. Figure 1 presents a comparison between the GC-MS chromatogram of sample 19 obtained during the 2018 and 2019 crop seasons. A higher number of volatiles was previously reported in the literature, e.g., by Boskou et al. [17], claiming the presence of about 280 volatile compounds in virgin olive oils (VOOs); similarly, 700 components were listed by Cecchi et al. [14]. However, to the best of our knowledge, this is the first study to detect such a high number of volatiles in Moroccan olive oils.

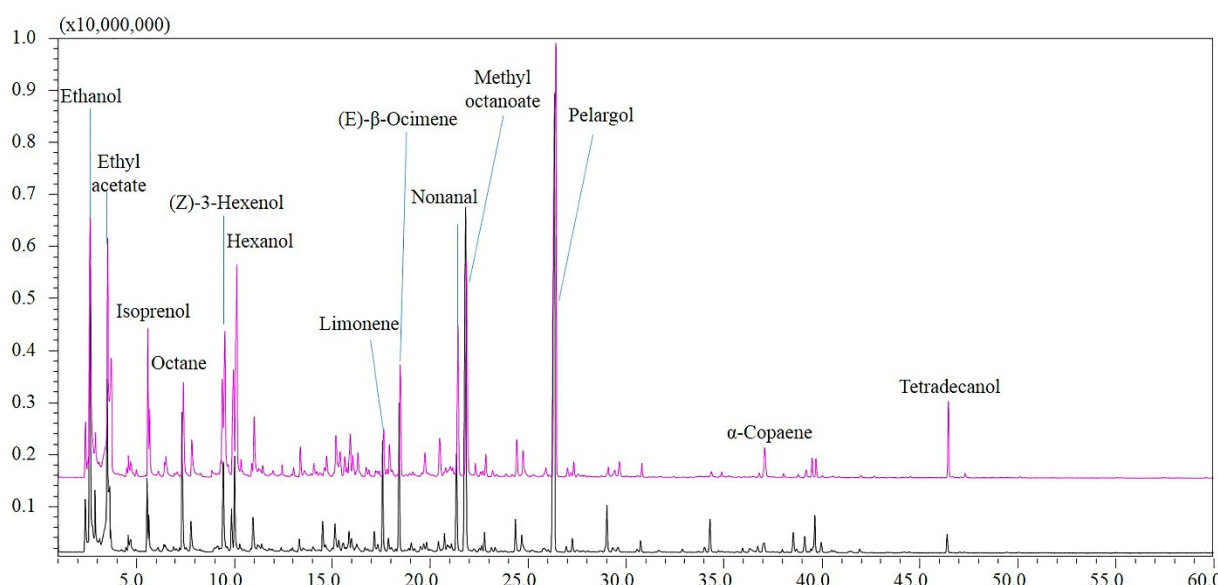


Figure 1. Comparison between GC-MS chromatogram of sample 19 obtained from the 2018 (black) and 2019 (pink) crop seasons.

Generally, the number of volatile compounds identified to date in Moroccan olive oils is modest. For instance, 35 volatiles were detected in 3 European olive varieties, “Arbosana”, “Arbequina”, and “Koroneiki”, cultivated in the oriental region of Morocco [39]; 40 compounds in olive oils “Picholine Marocaine” from 7 north Moroccan regions [23]; and 84 in oils produced in Eastern Morocco [40]. The latter figure shows a slight similarity with those produced in Algeria (78 compounds) [41]. Nevertheless, a total of 14 and 10 volatiles were reported in another Algerian study, for “Souidi” and “Zeletni” EVOOs, respectively [42]. On the other hand, by using GC-MS examination, Flath et al. [18] identified 77 polar volatile components. Similarly, 65 and 56 volatiles were detected in some European VOOs [43,44] and 5 Greek cultivars [19], respectively.

All the identified volatiles in this study were classified into nine main groups (Table 1): terpenes, hydrocarbons, furans, esters, alcohols, acids, ketones, aldehydes, and nitrogen compounds. In the literature, different chemical classes were revealed in olive oil samples. For instance, five major groups (aldehydes, alcohols, esters, terpenes, and organic acids) were identified in Dalmatian olive oils (Croatia) [6], six classes (aldehydes, alcohols, esters, ketones, hydrocarbons, and carboxylic acids) in Moroccan olive oils [23,40], and seven groups were observed in other VOOs [19,43,44]: aldehydes, alcohols, hydrocarbons, acids, ketones, and esters were the common detected groups; however, furans were characterized in some European VOOs [43,44], and ethers in some Greek VOOs [19].

In both seasons (2018/19 and 2019/20), alcohols were the main volatile classes in the studied olive oil samples, followed by terpenes. However, to some extent, this result does not support the previous research where C6 compounds, mostly C6 aldehydes (hexanal, Z-3-hexenal, and E-2-hexenal), C6 alcohols (hexanol, Z-3-hexenol, and E-2-hexenol), and C6 esters (hexyl acetate and Z-3-hexenil acetate) [6] that principally originate from linoleic and linolenic acids through the lipoxygenase pathway [39,41], were the major groups along with hydrocarbons [19,45]. In fact, in comparison with aldehydes, alcohols have weaker sensory importance; however, they are related to positive sensory attributes in olive oils [6]. Unlike what we observed, terpenes (especially sesquiterpenes), which are known as markers to distinguish olive oils from different varieties and geographical origins [46], ranged from 0.72 to 5.18% in some Turkish olive oils [26].

Table 1. The nine volatile groups detected in Moroccan VOOs (2018/19 and 2019/20) expressed in area % as average $\pm$ SD of three measurements by GC-FID analysis.

Components	Geographical Area																			
	Sp1	Sp2	Sp3	Sp4	Sp5	Sp6	Sp7	Sp8	Sp9	Sp10	Sp11	Sp12	Sp13	Sp14	Sp15	Sp16	Sp17	Sp18	Sp19	
Alcohols	2018	34.54 ^{hi} ± 1.12	30.44 ^{ab} ± 0.61	32.01 ^{ah} ± 1.04	31.68 ^{ah} ± 1.03	36.30 ^{fi} ± 1.18	36.95 ^{fi} ± 1.20	41.13 ^{de} ± 1.34	27.7 ^b ± 0.90	34.69 ^{hi} ± 1.13	29.20 ^{ab} ± 0.95	45.44 ^c ± 1.48	42.50 ^{cde} ± 1.38	40.84 ^{de} ± 1.33	38.98 ^{df} ± 1.27	42.79 ^{ce} ± 1.24	43.90 ^{ce} ± 1.43	50.48 ^g ± 1.24	51.38 ^g ± 1.50	46.05 ^c ± 1.39
	2019	39.22 ^{dh} ± 1.31	32.62 ^{ac} ± 1.09	40.11 ^{dhi} ± 1.34	46.91 ^{gij} ± 1.57	54.52 ^b ± 1.82	39.98 ^{dhi} ± 1.34	40.97 ^{efh} ± 1.37	38.87 ^{dh} ± 1.30	45.34 ^{egij} ± 1.52	28.37 ^a ± 0.50	56.92 ^b ± 1.90	36.50 ^{cd} ± 1.22	43.06 ^{efgh} ± 0.40	53.01 ^b ± 1.77	56.32 ^b ± 1.88	54.66 ^b ± 1.57	47.54 ^{ij} ± 1.59	48.50 ⁱ ± 1.62	44.02 ^{efg} ± 1.22
Terpenes	2018	28.47 ⁱ ± 0.93	22.77 ⁱ ± 0.68	14.18 ^g ± 0.46	18.49 ^{ac} ± 0.60	12.96 ^{fg} ± 0.42	17.82 ^{abce} ± 0.58	20.44 ^d ± 0.67	17.6 ^{abce} ± 0.57	16.22 ^e ± 0.53	18.28 ^{abc} ± 0.59	18.94 ^{ad} ± 0.62	17.06 ^{bce} ± 0.56	12.07 ^f ± 0.39	19.34 ^{ad} ± 0.63	16.58 ^{be} ± 0.54	19.11 ^{ad} ± 0.62	13.46 ^{fg} ± 0.54	13.98 ^g ± 0.45	25.94 ^h ± 0.84
	2019	31.94 ^k ± 1.03	18.60 ^{hi} ± 0.60	18.34 ^{dh} ± 0.59	20.53 ⁱ ± 0.66	17.49 ^{cdh} ± 0.57	16.67 ^{bcdh} ± 0.59	24.67 ^{aj} ± 0.80	26.57 ^j ± 0.86	15.76 ^{bc} ± 0.51	23.37 ^a ± 1.04	16.56 ^{bcd} ± 0.54	39.09 ^e ± 1.26	15.15 ^{bf} ± 0.67	12.99 ^g ± 0.42	15.98 ^{bc} ± 0.52	16.38 ^{bcd} ± 0.40	12.67 ^g ± 0.41	13.31 ^{fg} ± 0.43	15.77 ^{bc} ± 0.51
Hydrocarbons	2018	7.26 ^c ± 0.24	12.44 ^h ± 0.40	2.96 ^g ± 0.10	4.91 ^{ef} ± 0.16	3.01 ^g ± 0.10	6.67 ^{bc} ± 0.22	3.13 ^g ± 0.10	18.0 ⁱ ± 0.59	9.62 ^a ± 0.31	8.89 ^a ± 0.29	9.66 ^a ± 0.31	6.65 ^{bc} ± 0.22	5.24 ^{de} ± 0.17	5.98 ^{bd} ± 0.19	4.22 ^f ± 0.14	6.07 ^b ± 0.20	7.15 ^c ± 0.14	2.89 ^g ± 0.09	5.91 ^b ± 0.19
	2019	6.82 ^{lj} ± 0.23	3.28 ^{hm} ± 0.11	2.85 ^m ± 0.10	9.16 ⁿ ± 0.31	5.29 ^{de} ± 0.18	7.20 ^j ± 0.10	3.69 ^{gh} ± 0.12	3.00 ^m ± 0.10	4.48 ^{fl} ± 0.15	10.36 ^a ± 0.35	6.07 ^{bc} ± 0.20	5.67 ^{bd} ± 0.19	5.04 ^{ef} ± 0.17	5.62 ^{bfe} ± 0.19	3.82 ^{gh} ± 0.13	6.88 ^{ij} ± 0.23	8.26 ^k ± 0.28	6.33 ^{ci} ± 0.21	4.06 ^{gl} ± 0.14
Esters	2018	3.86 ^h ± 0.13	2.57 ^d ± 0.08	9.83 ^{bcd} ± 0.32	10.68 ^{ae} ± 0.35	7.27 ^j ± 0.24	8.37 ^g ± 0.27	4.22 ^h ± 0.14	4.27 ^h ± 0.14	11.08 ^e ± 0.36	10.26 ^{abc} ± 0.33	2.74 ^d ± 0.09	10.46 ^{abe} ± 0.34	9.10 ^{fg} ± 0.30	9.54 ^{cf} ± 0.31	9.39 ^f ± 0.31	9.70 ^{bcd} ± 0.32	3.54 ^h ± 0.31	6.14 ⁱ ± 0.20	5.50 ⁱ ± 0.18
	2019	6.56 ^{ej} ± 0.22	4.72 ^{cd} ± 0.16	9.31 ^a ± 0.31	7.36 ^{gj} ± 0.25	5.09 ^{bc} ± 0.17	12.42 ^h ± 0.31	6.47 ^{ej} ± 0.22	6.44 ^{ej} ± 0.22	9.71 ^a ± 0.32	9.37 ^a ± 0.31	4.83 ^{bcd} ± 0.16	5.67 ^{bce} ± 0.19	25.63 ^f ± 0.61	8.23 ^g ± 0.28	7.83 ^g ± 0.26	5.70 ^{be} ± 0.19	4.11 ^d ± 0.14	11.72 ^h ± 0.39	16.02 ⁱ ± 0.54
Aldehydes	2018	10.68 ^{cd} ± 0.35	17.86 ⁱ ± 0.58	12.70 ^j ± 0.41	10.12 ^{cd} ± 0.33	20.53 ^k ± 0.67	14.35 ^a ± 0.47	16.29 ^b ± 0.53	15.1 ^{ab} ± 0.49	7.09 ^{fh} ± 0.23	15.18 ^{ab} ± 0.49	9.92 ^{cd} ± 0.32	4.61 ^e ± 0.15	8.18 ^f ± 0.27	9.78 ^c ± 0.32	11.11 ^d ± 0.36	6.77 ^{gh} ± 0.22	10.28 ^{cd} ± 0.36	9.50 ^c ± 0.20	5.75 ^{eg} ± 0.19
	2019	5.38 ^e ± 0.18	19.36 ^g ± 0.65	5.27 ^e ± 0.18	6.23 ^h ± 0.21	3.45 ^{bd} ± 0.12	7.05 ⁱ ± 0.18	9.56 ^j ± 0.32	8.52 ^k ± 0.28	4.07 ^{bc} ± 0.14	12.63 ^a ± 0.11	4.15 ^{bc} ± 0.14	3.47 ^{bd} ± 0.12	3.63 ^{bd} ± 0.12	2.93 ^d ± 0.10	3.12 ^d ± 0.10	3.21 ^d ± 0.11	5.31 ^e ± 0.18	4.49 ^c ± 0.15	11.34 ^f ± 0.38
Acids	2018	4.11 ⁱ ± 0.13	4.45 ^{gi} ± 0.14	17.83 ^d ± 0.58	10.73 ^c ± 0.35	7.19 ^e ± 0.23	5.94 ^{fh} ± 0.19	2.66 ^b ± 0.09	4.44 ^{gi} ± 0.14	15.05 ^g ± 0.49	9.11 ^a ± 0.30	2.47 ^b ± 0.08	11.10 ^c ± 0.36	17.82 ^d ± 0.58	6.79 ^{ef} ± 0.22	8.58 ^a ± 0.28	8.64 ^a ± 0.28	8.90 ^a ± 0.28	10.31 ^c ± 0.34	5.18 ^{gh} ± 0.17
	2019	3.33 ^b ± 0.11	9.63 ^e ± 0.32	17.64 ^g ± 0.59	3.54 ^b ± 0.12	7.53 ^{dh} ± 0.25	8.05 ^h ± 0.59	2.19 ^f ± 0.07	2.41 ^f ± 0.08	13.32 ⁱ ± 0.45	5.11 ^a ± 0.17	3.58 ^b ± 0.12	3.91 ^b ± 0.13	3.52 ^b ± 0.12	11.17 ^c ± 0.37	6.80 ^d ± 0.23	5.35 ^a ± 0.18	5.38 ^a ± 0.18	9.73 ^e ± 0.33	2.42 ^f ± 0.08
Ketones	2018	4.48 ⁱ ± 0.15	4.62 ^{hi} ± 0.15	5.83 ^j ± 0.19	4.99 ^{hk} ± 0.16	4.98 ^{hk} ± 0.16	4.66 ^{hi} ± 0.15	7.38 ⁱ ± 0.24	5.18 ^k ± 0.17	2.36 ^e ± 0.08	4.03 ^a ± 0.13	3.40 ^{bc} ± 0.11	1.09 ^d ± 0.04	2.16 ^e ± 0.07	3.64 ^{ab} ± 0.12	3.24 ^c ± 0.11	1.46 ^{df} ± 0.05	2.13 ^{eg} ± 0.11	1.74 ^{fg} ± 0.06	1.14 ^d ± 0.04
	2019	2.30 ^{hj} ± 0.08	5.38 ^g ± 0.18	1.77 ^c ± 0.06	2.14 ^{dh} ± 0.07	2.91 ^f ± 0.10	2.72 ^{fi} ± 0.06	2.52 ^{ij} ± 0.08	2.58 ⁱ ± 0.09	2.05 ^{dh} ± 0.07	4.84 ^a ± 0.16	1.51 ^b ± 0.05	1.95 ^{cd} ± 0.07	0.90 ^e ± 0.03	0.99 ^e ± 0.03	1.40 ^b ± 0.05	1.35 ^b ± 0.05	2.97 ^f ± 0.10	1.32 ^b ± 0.04	1.04 ^e ± 0.03

Table 1. Cont.

Components		Geographical Area																		
		Sp1	Sp2	Sp3	Sp4	Sp5	Sp6	Sp7	Sp8	Sp9	Sp10	Sp11	Sp12	Sp13	Sp14	Sp15	Sp16	Sp17	Sp18	Sp19
Furans	2018	0.63 ^{ef} ±	1.84 ^h ±	0.59 ^e ±	1.75 ^{hi} ±	1.67 ^{ci} ±	0.76 ^{af} ±	0.80 ^a ±	3.36 ^j ±	0.60 ^e ±	0.81 ^a ±	1.60 ^{bc} ±	1.36 ^d ±	0.65 ^{ef} ±	1.53 ^b ±	0.32 ^g ±	0.64 ^{ef} ±	0.68 ^{ae} ±	0.43 ^g ±	0.44 ^g ±
		0.02	0.06	0.02	0.06	0.05	0.02	0.03	0.11	0.02	0.03	0.05	0.04	0.02	0.05	0.01	0.02	0.01	0.01	0.01
	2019	0.66 ^j ±	0.48 ^g ±	0.15 ^{bcd} ±	0.17 ^f ±	0.17 ^f ±	0.24 ^d ±	0.14 ^{bcd} ±	0.38 ⁱ ±	0.37 ^{hi} ±	0.72 ^a ±	0.12 ^b ±	0.13 ^{bc} ±	0.25 ^{de} ±	0.12 ^b ±	0.24 ^d ±	0.16 ^{ef} ±	0.51 ^g ±	0.28 ^e ±	0.34 ^h ±
		0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.00	0.00	0.01	0.00	0.01	0.01	0.02	0.01	0.01
Nitrogen compounds	2018	1.09 ^{cef} ±	1.13 ^{bce} ±	0.71 ^a ±	0.77 ^{ag} ±	0.81 ^{ag} ±	0.58 ⁱ ±	1.00 ^f ±	1.17 ^{bcd}	0.87 ^g ±	0.71 ^a ±	1.17 ^{bcd}	1.12 ^{bce} ±	1.05 ^{ef} ±	0.87 ^g ±	1.10 ^{bce} ±	1.25 ^{dh} ±	1.34 ^h ±	1.19 ^{bd} ±	1.33 ^h ±
		0.04	0.04	0.02	0.02	0.03	0.02	0.03	± 0.04	0.03	0.02	± 0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.04	0.04
	2019	0.61 ^{di} ±	0.48 ^e ±	1.43 ^h ±	0.79 ^{cf} ±	0.64 ⁱ ±	0.65 ^{gi} ±	0.59 ^{di} ±	0.57 ^{dei} ±	1.17 ^{bj} ±	0.97 ^a ±	1.01 ^a ±	1.24 ^b ±	0.86 ^c ±	0.53 ^{de} ±	0.74 ^{fg} ±	1.41 ^h ±	0.61 ^{di} ±	0.87 ^c ±	1.11 ^j ±
		0.02	0.02	0.05	0.03	0.02	0.05	0.02	0.02	0.04	0.03	0.03	0.04	0.03	0.02	0.02	0.05	0.02	0.03	0.04
Total volatiles	2018	95.11	98.67	96.65	94.12	94.71	96.10	97.02	96.98	97.56	96.46	95.35	95.96	97.09	96.42	97.44	97.52	97.86	97.80	97.31
	2019	96.81	94.56	96.87	96.83	97.09	94.98	90.79	89.34	96.27	95.74	94.75	97.63	98.04	95.60	96.26	95.12	87.36	96.55	96.13

^{a–n} Average ± SD (n = 3). Different superscript letters in the same row indicate significant differences between EVOOs from different sampling sites ($p < 0.05$).

In the current research, pelargol, *n*-hexanol, (*Z*)-3-hexenol, (*E*)-2-hexenol, and ethanol are the predominant alcohols used. Among them, (*Z*)-3-hexenol has been reported to possess a green banana note [47]. Similarly, (*Z*)-3-hexenol, hexanol, and ethanol were the major detected alcohols in some Moroccan olive oils [40]. Moreover, ethanol (fermented-like, ripe-fruit note) was observed in higher concentrations in olive oils produced in Greece (“Ntopia” cultivar) [45]. Besides, three of the most prevalent alcohols in our olive oils were mainly derived from polyunsaturated fatty acids through the LOX pathway; *n*-hexanol is formed from linoleic acid, but (*Z*)-3-hexenol and (*E*)-2-hexenol are mainly produced from linolenic acid [4,29]. Additionally, the result shows that (*E*)-4,8-dimethyl-nona-1,3,7-triene, limonene, and (*E*)- β -ocimene are the most prevalent terpenes, with average values of 7.55%, 3.22%, and 2.29% in 2018’s olive oils vs. 5.29%, 4.42%, and 3.95% in 2019’s samples, respectively. Comparatively, limonene was the major terpene in a new Tunisian EVOO (“Meski” variety) [48] analyzed by using HS-SPME/GC-MS.

By comparing hydrocarbons in both seasons, mesitylene (1.77%) and (*E*)-3-ethyl-1,5-octadiene (1.17%) were the predominant hydrocarbons in 2018’s oils; however, styrene (1.81%), *n*-undecane (1.73%), and *n*-octane (1.43%) were the major hydrocarbons in oils from 2019. Similarly, ketones were represented by 6-methyl-5-hepten-2-one (0.83%) and hexyl methyl ketone (0.61%) in 2018’s oil, and by 3-octanone (0.53%) and 6-methyl-5-hepten-2-one (0.49%) in oils from the 2019 crop yield. On the other hand, ethyl acetate was the most abundant ester in the 2018 and 2019 seasons with averages of 2.73% and 2.81%, respectively. In this regard, while comparing Italian, Moroccan, and Spanish olive oils, Reiners and Grosch [8] asserted that Moroccan EVOOs are rich in fruity esters, such as ethyl isobutyrate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, and ethyl cyclohexylcarboxylate.

In addition, *n*-nonanal followed by *n*-hexanal and (*E*)-2-hexenal (not detected in 2019 samples) related, respectively, to citrus-like, green, and green apple-like odor [8] were the most prevalent aldehydes in the studied olive oils. Contrary to expectations, these results differ from some published studies [6,26,31] that proved the abundance of (*E*)-2-hexenal followed by hexanal [26]. The latter hexanal and (*E*)-2-hexenal are the LOX pathway products [4,29]. (*E*)-2-Hexenal is produced from the 13-hydroperoxide of linolenic acid that is cleaved by hydroperoxide lyase to form 3-hexenal, which in turn might be reduced to (*Z*)-3-hexenol [4,49], whereas *n*-hexanal is produced by the involvement of the hydroperoxide lyase (HPL) that cleaves the 13-hydroperoxide of linoleic acid [4]. Within the context, *n*-hexanal was positively correlated with linoleic acid (Table S3) in our olive oil samples. Along with this C6 aldehyde, a C5 aldehyde (*E*)-2-pentenal exhibited a positive correlation with linolenic acid indicating an increase in the secondary pathway’s activity in olive oils rich in linolenic acid [49].

On the other hand, acetic (5.72% vs. 5.38%) and formic (1.66% vs. 0.89%) acids were the highest acids in both seasons (2018 vs. 2019), respectively. Moreover, with an average of 0.33% vs. 0.08%, 5-ethyl-2(5H)-furanone was the predominant furan in olive oils in both seasons.

3.2. Season Impact

As can be observed in Figure 2, the percentage of total volatiles in the 2018 season (96.64%) is slightly higher than that of 2019 (95.09%), along with the ranges of total volatiles that are 94.12–98.67% and 87.36–98.04% during the 2018 and 2019 seasons, respectively (Table 1). Similarly, the variability of total volatiles in oils obtained from different seasons (2017 and 2018) was observed by Polari et al. [34].

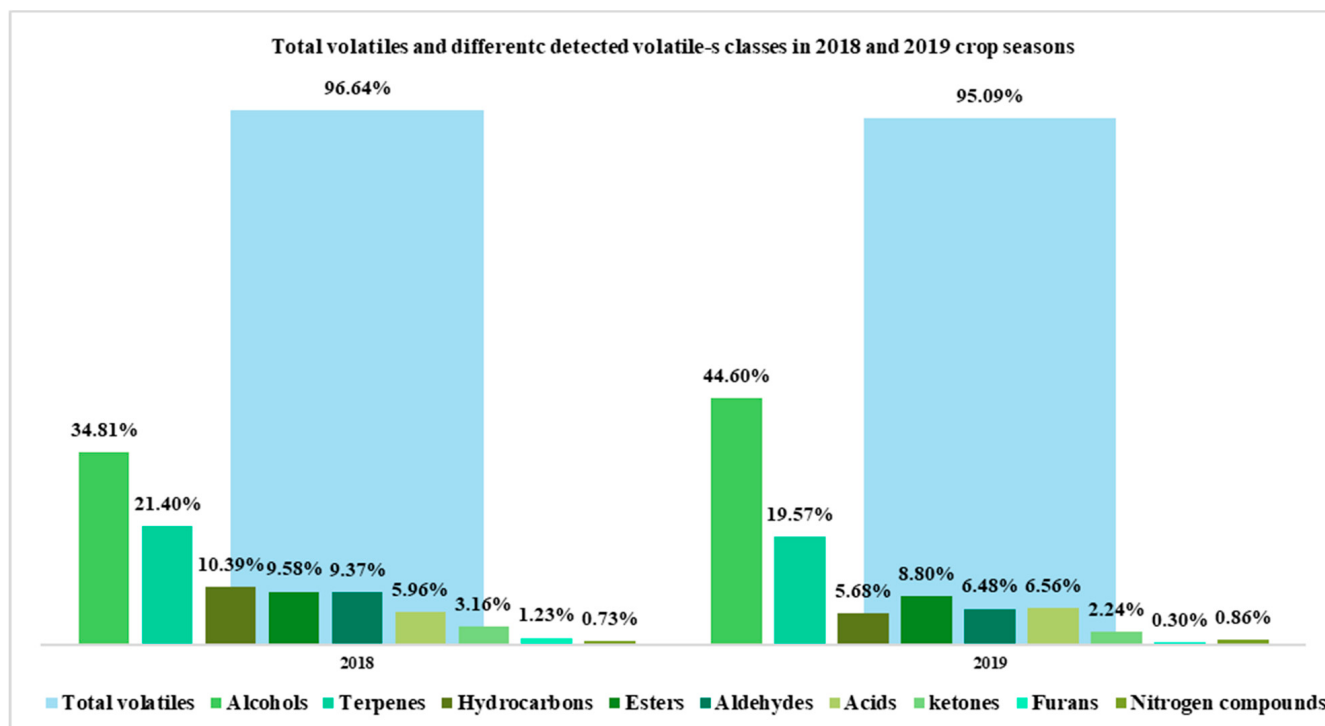


Figure 2. Overlapping bar chart showing the average of total volatiles and the detected volatile classes in the 2018 and 2019 crop seasons.

Alcohols and terpenes were the predominant volatile groups in olive oils obtained from the two studied crop years. However, the other volatile classes in both seasons were in different abundance orders: hydrocarbons (10.39%) followed by esters (9.58%), aldehydes (9.37%), acids (5.96%), ketones (3.16%), furans (1.23%), and nitrogen compounds (0.73%) in 2018/19 olive oils, while esters (8.80%) were followed by acids (6.56%), aldehydes (6.48%), hydrocarbons (5.68%), ketones (2.24%), nitrogen compounds (0.86%), and furans (0.30%) in olive oils obtained in 2019/20. As can be observed, the 2018 olive oils contain a similar amount ($\approx 10\%$) of hydrocarbons, esters, and aldehydes; however, in comparison, these oils contain about 2 times more hydrocarbons (10.39% vs. 5.68%) than those produced in the 2019 crop year.

Taken together, the variability of the volatile composition between the studied harvest seasons matches those observed in earlier studies [50]. These results might be elucidated by the diverse climate conditions throughout the harvest season [22], including the substantial role of the water status of the olive tree during the crop year. In detail, Fernandes-Silva et al. [51] observed that the irrigation regime affected volatiles in olive oils produced in the driest years, but not those from years with a rainy spring.

3.3. Geographical Origin Influence

Considering the strong relationship between the geographical origin and volatile compounds in olive oils [26,28,52,53], in this work, the nine detected volatile groups and sampling sites, viz., Sp1 to Sp19, belonging to five Moroccan administrative regions were subjected to an interactive heatmap (Figure 3) to highlight the abundance and distribution of volatiles according to the geographical origin.

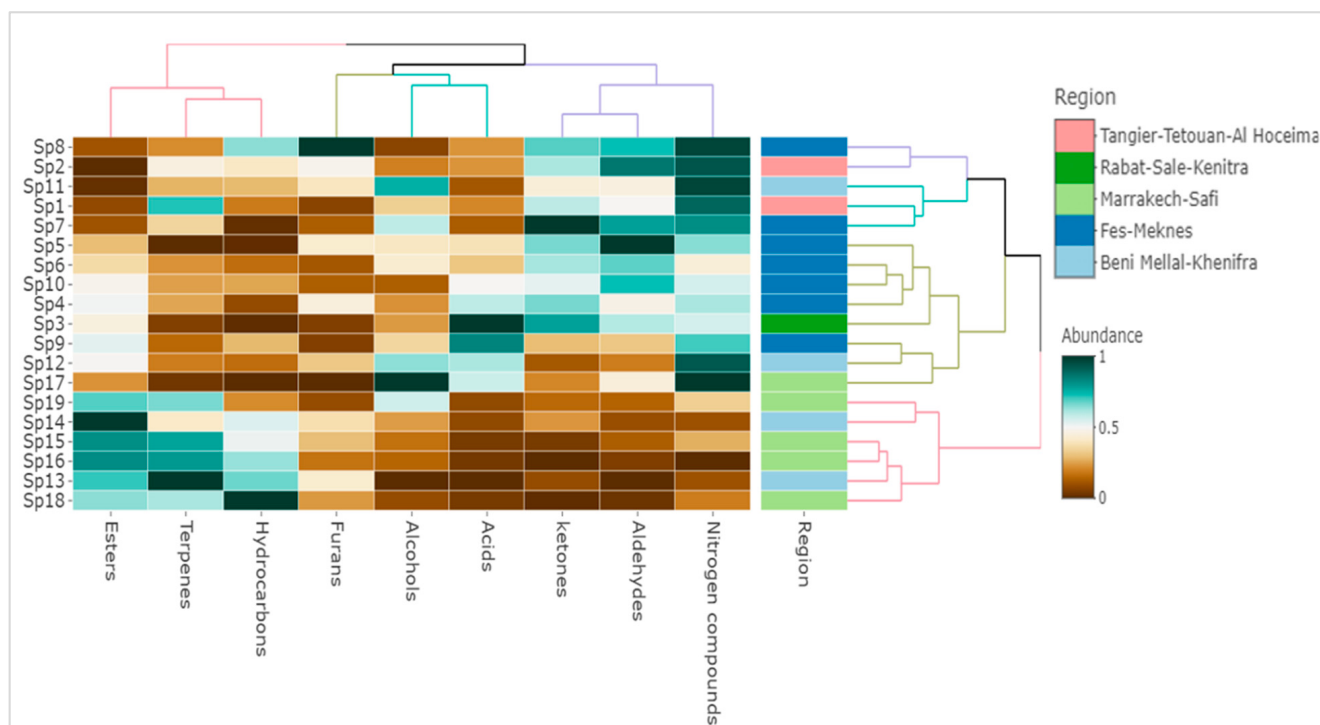


Figure 3. Interactive heatmap based on the identified volatile classes in nineteen Moroccan olive oils from the 2018/19 crop year. Brown and teal boxes show lower and higher quantities of volatile compounds, respectively. Data were normalized and the plotly method was used.

From the heatmap (Figure 3), we can observe that olive oils from the Marrakech-Safi region (except Sp17) and two samples (Sp13 and Sp14) from the Beni Mellal-Khenifra region were the poorest in nitrogen compounds, aldehydes, ketones, acids, alcohols, and furans, whereas it turned out to be the richest in hydrocarbons, esters, and terpenes. In fact, as the Beni Mellal-Khenifra region is located in the northeast of the Marrakech-Safi region, these results could be explained by the geographical proximity. On the other hand, olive oils from the northern Moroccan regions were generally rich in nitrogen compounds, aldehydes, and ketones; however, poor in acids, alcohols, furans, hydrocarbons, terpenes, and esters. Substantial dissimilarities in volatile classes based on the geographical areas of olive oil were also observed by Eriotou et al. [45].

On the other hand, it can be observed that some olive oils were not classified depending on their region of origin. For instance, Sp11 (Beni Mellal-Khenifra) and Sp8 (Fes-Meknes) were grouped with olive oils from far-northern Morocco (Tangier-Tetouan-Al Hoceima). However, Sp8 olive oil was distinguishable by the poor level of esters against modest concentrations in oils produced in the same region (Fes-Meknes). Yet, it revealed a high concentration of furans and nitrogen compounds against low and modest amounts, respectively. Remarkably, Sp3 was grouped with olive oils from the Fes-Meknes region, which is located next to the Rabat-Sale-Kenitra region (Sp3) along the west side, whilst it appeared distinguishable by the high percentage of acids.

Bearing in mind the considerable role of the enzymatic activity in the volatiles' formation, the observed increase in esters in olive oils from the regions of Beni Mellal-Khenifra and Marrakech-Safi could be attributed to the high activity of alcohol dehydrogenase (ADH) and alcohol acetyl transferase (AAT) enzymes. The ADH reduces the C6 aldehydes to the corresponding alcohols, which in turn are transferred to the corresponding esters by the activity of AAT. Indeed, the simultaneous variability in the levels of aldehydes and esters in all olive oils suggest the influence of environmental growth conditions of the olive tree on the activity of ADH and AAT. Therefore, our findings imply that the activity of these enzymes in the "Picholine Marocaine" cultivar depends on the pedoclimatic conditions

of the area of origin. These results are consistent with those of Baccouri et al. [54], but contrast with the observation of Kalua et al. [1] who claimed that the activity of AAT is less dependent on climatic conditions. Furthermore, our findings satisfactorily fit with other results regarding ADH activity [48,53].

In addition, by comparing the profile of volatiles in terms of acid, alcohol, and furan amounts, it appeared that, except for some samples that exhibited higher concentrations, all the other olive oils presented similar levels. However, the other volatile groups, nitrogen compounds, aldehydes, and ketones against hydrocarbons, esters, and terpenes apparently seemed to be chemical markers distinguishing olive oils from different growing areas. In fact, these results match those observed in earlier studies where some volatiles, such as hydrocarbons [48,54] and terpenes [13,46], were considered as geographical markers that might differentiate olive oils produced from different geographical origins and aid their traceability.

Overall, substantiating precedent studies exhibiting the strong variability in the volatile fraction of olive oil from different growing areas [26,45,54,55], the interactive heatmap (Figure 2) revealed a clear classification of Moroccan olive oils according to their origin of provenance. It seems possible that this discrimination is mainly due to the weather conditions and soil composition that distinguish each sampling site.

3.4. *Pedo-Climatic Conditions*

Given that dissimilarities in volatile composition are attributed to several factors, such as the geographical origin, which is known as the main factor influencing the qualitative profiles of volatile compounds in olive oils [6,23,41,42], evaluating the set of factors related to the geographical origin of production is fundamental for olive oil's discrimination [56]. Hence, in this section, the focus was principally on investigating the impact of the diverse environmental conditions of origin, mainly soil, climate, and geographical coordinates, on the volatile profile of monovarietal "Picholine Marocaine" Moroccan olive oils. For this purpose, alongside the heatmap (Figure 2), a correlation matrix was plotted to highlight any potentially existing connections between the various studied variables. Nevertheless, as a matter of fact, due to the considerable number of identified volatiles, the correlational analysis presented in Table 2 was based on the volatile groups, total volatiles, and geographical zone variables (10×22). The edaphic conditions of the studied zones are provided in Table S4.

Except for furans and total volatiles, all the other volatile groups were influenced by seven geographical origin variables. With regard to the climatic conditions, acids ($r = 0.46$), aldehydes, and ketones ($r = 0.79$) tended to increase with the total rainfall, whereas terpenes, hydrocarbons, and esters ($r = -0.47$, $r = -0.50$ and $r = -0.52$, respectively) tended to decrease with a higher amount of rainfall. Indeed, it is widely known that the regime of water leads to some influence on the volatile fraction [32]. In this ambit, despite the non-significant correlation between total volatile and cumulative rainfall ($r = -0.43$), these results corroborate to a certain extent with some findings where the availability of water leads to the diminishing of volatiles in olive fruit [6], and in the produced olive oils (case of irrigation) [33]. Nonetheless, our results do not support other observations about the positive correlation between cumulative rainfall and total volatiles (except hexanal and isobutyl acetate) [57].

Additionally, ketones were positively impacted by the relative humidity ($r = 0.51$). Interestingly, this evidence points to some extent the role of climatic conditions, including relative humidity, to distinguish olive oils based on the volatile composition [26]. However, our observation regarding the other climatic variables does not lend support to what was previously revealed on temperature [26,28,31] and windiness (the wind speed) effects [58].

Table 2. Correlation matrix showing the Pearson’s correlation of volatile classes, pedo-climate, and geographical origin variables.

Geographical Origins Variables	Volatile Classes									
	Alcohols	Terpenes	Hydrocarbons	Esters	Aldehydes	Acids	Ketones	Furans	Nitrogen Compounds	Total Volatiles
Rainfall	−0.14	−0.47 *	−0.50 *	−0.52 *	0.79 ****	0.46 *	0.79 ****	0.11	0.45	−0.43
Temperature	−0.11	0.02	−0.01	0.11	0.09	−0.05	0.06	−0.01	−0.17	0.15
Wind speed	0.11	0.11	0.08	0.2	−0.17	−0.14	−0.18	−0.24	−0.22	0.33
Relative humidity	−0.02	−0.15	−0.3	−0.42	0.44	0.19	0.51 *	−0.06	0.32	−0.18
Clay	−0.01	−0.06	−0.09	−0.31	0.25	0.04	0.28	0.11	0.27	−0.06
Silt	−0.31	0.14	0.25	0.53 *	−0.35	0.03	−0.31	0.13	−0.38	0.18
Sand	0.46 *	−0.03	−0.25	−0.27	0.01	−0.07	0.03	−0.26	0.18	−0.27
pH	−0.13	−0.12	0.28	0.39	−0.11	−0.06	−0.28	0.17	−0.36	0.4
Conductivity	0.01	0.06	0.44	0.11	−0.26	−0.19	−0.33	−0.1	−0.18	0.38
Organic matter	−0.22	0.15	−0.14	0.12	0.12	−0.15	0.3	−0.1	−0.23	−0.36
Limestone	−0.29	−0.18	0.14	−0.15	0.41	0.03	0.22	0.12	0.05	0.28
N	−0.2	0.22	−0.04	−0.07	0.17	−0.32	0.32	0.34	−0.04	−0.2
P	0.19	0.04	−0.23	−0.3	0.17	−0.09	0.41	−0.15	0.19	0.03
K	−0.13	0.08	0.15	0.23	−0.14	−0.22	0.02	0.3	−0.28	−0.15
Ca ²⁺	−0.35	−0.17	0.11	0.09	0.3	−0.05	0.25	0.41	−0.14	0.06
Mg ²⁺	0.05	0.12	0.23	0.18	−0.32	−0.12	−0.38	0.24	0.01	0.15
Na ⁺	−0.17	0.2	0.58 **	0.23	−0.38	−0.25	−0.41	−0.09	−0.33	0.31
K ⁺	−0.17	0.09	0.14	0.12	−0.05	−0.23	0.12	0.32	−0.23	−0.15
C/N	−0.23	−0.1	−0.08	0.2	0.09	0.25	0.09	−0.4	−0.2	−0.14
Latitude	−0.15	−0.37	−0.44	−0.64 **	0.79 ****	0.38	0.85 ****	0.14	0.53 *	−0.35
Longitude	−0.11	−0.41	−0.38	−0.50 *	0.67 **	0.34	0.74 ***	0.2	0.46 *	−0.39
Altitude	0.08	0.14	0.13	0.03	−0.26	−0.03	−0.34	−0.19	0.09	−0.1

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$.

Concerning the pedologic conditions, three positive correlations occurred between (silt percentage $\times$ esters, $r = 0.53$), (alcohols $\times$ sand, $r = 0.46$), and (hydrocarbons $\times$ exchangeable sodium, $r = 0.58$). To some extent, our results appear to corroborate with those of Ben Rached et al. [29] who noted that 1-hexanol, which is one of the five prevalent alcohols in our olive oils, was the major compound in olive oils from sandy soils, but soil limestone provided olive oils rich in 2-hexenal. In fact, the latter was not well substantiated by our observation because none of the positive correlations, limestone percentage $\times$ hexenal (data not shown) and limestone percentage $\times$ aldehydes (Table 2), were statistically significant.

Interestingly, the influence of the soil texture on volatile compounds provides an important insight into the role of this mineral fraction in supplying the required elements for the plant's growth. It is also the reason for the variability of C6 aldehydes and alcohols, which suggests the impact of the different pedologic conditions on ADH's activity [48]. In the literature, other edaphic variables showed their influence on the volatile fraction of olive oil. By studying the effect of salt (NaCl) treatment on olive oil's quality, Cresti et al. [59] observed the positive impact of salinity on alcohol composition (namely, aliphatic and triterpenic alcohols). In addition, Ranalli et al. [58] asserted the negative influence of soil's C/N ratio on the fruitiness of the produced olive oil, whereas no significant correlation between these soil variables and the nine studied volatile groups was detected.

Moreover, significant correlative links between the geolocalization parameters (latitude and longitude) and four volatile groups were recorded. Esters were negatively affected by the latitude ($r = -0.64$) and longitude ($r = -0.50$), while aldehydes, ketones, and nitrogen compounds were positively affected by latitude ($r = 0.79$, $r = 0.85$, $r = 0.53$) and longitude ($r = 0.67$, $r = 0.74$, $r = 0.46$). This satisfactorily fits with the results of Kiralan et al. [26] who observed that the formation of volatiles (notably (*E*)-2-hexenal) in olive oils is affected by the geographical area of origin, namely, latitude and longitude. Despite the fact that other geographical origin factors, such as altitude and temperature, modify the enzymatic activities of volatiles [60], in the current study, no correlation was observed between the volatile fraction and these variables.

Taken together, similar to anterior findings [48,61], our results suggest that there is a considerable association between the volatile profile of olive oil and the environmental conditions, especially the edaphoclimatic factors, latitude, and longitude.

4. Conclusions

The present work was undertaken to screen the volatile profile and evaluate the impact of the crop season and environmental conditions on the sensory characteristics of thirty-eight Moroccan olive oils ("Picholine Marocaine") produced in nineteen sampling sites. Through this investigation, more than two hundred volatile compounds were identified in olive oils produced during two successive crop years (2018/19 and 2019/20). These volatiles were classified into nine major groups: terpenes, hydrocarbons, furans, esters, alcohols, acids, ketones, aldehydes, and nitrogen compounds. Moreover, the crop year of olive oil's production exhibited a considerable impact on the composition of volatile compounds, and this variability might be mainly caused by the climate conditions, e.g., water status in each harvest season. Furthermore, the heatmap highlighted a clear classification of volatile groups according to geographical origin, which suggests the dependence of the enzymatic activity, such as ADH, and the AAT enzymes on the pedoclimatic conditions of the region of origin. In this regard, the correlation test provided further evidence highlighting the edaphoclimatic variables (mainly the rainfall and soil texture) that contribute the most to the variability of the volatile profile in Moroccan olive oils. As well, it demonstrated the considerable influence of latitude and longitude on four volatile groups (esters, aldehydes, ketones, and nitrogen compounds), which supports the notable role of the origin zone in producing olive oil with distinct attributes.

Overall, our study led us to conclude that, generally, the volatile profile in Moroccan olive oils depends on several external factors, mainly those related to the region of provenance and harvest season. Through this research, the importance of these variables was

underlined; however, future studies on the current topic are therefore recommended in order to establish a good comprehension of the involved factors.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/horticulturae8100925/s1>, Table S1: Volatile compounds in 2018 Moroccan VOOs expressed in area % as average $\pm$ SD of three measurements by GC-FID analysis, Table S2: Volatile compounds in 2019 Moroccan VOOs expressed in area % as average $\pm$ SD of three measurements by GC-FID analysis, Table S3: Association between the fatty acids profile and volatile compounds in Moroccan olive oils of 2018/19 crop season, Table S4: Results of the edaphic variables in the studied areas.

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