A theoretical approach for the impact of adulteration on the shelf life of olive oils

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Abstarct

The adulteration of olive oils with lower quality ones is an additional factor impacting oxidation evolution. The selected packaging material along with the storage conditions have a combinatorial impact, too. The combined system of olive oil-packaging-environment lead to a flavour profile, including hexanal, impacting the consumers' acceptance and quality appreciation. So far, the effect of packaging and environment have been studied both experimentally and theoretically for the shelf life yet not in combination to mixtures of olive oils. This work aims in providing a quick and reliable tool for distinguishing adultered extra virgin olive oils, based on their shelf life as affected by oxidation. The approach is based on using known packaging and environment related factors, but testing altered extra virgin olive oil compositions. By doing so, we propose the use of a predictive model in order to estimate the possibility of food to reach the end of its shelf life while the deviations of this possibility between refence and tested samples indicate potential adulteration. It is clearly showed that greater deviations correspond to higher assurance for a non-pure, adultered, extra virgin olive oil.

Keywords: adulteration, modeling, shelf life, olive oil, packaging, storage.

1. Introduction

Food adulteration has been led mostly by intercontinental antagonism, retail, profit issues and naïve consumers, worldwide. Both relative unions/associations and individual countries have been trying to prevent the food adulteration with legal frameworks. a need for advanced techniques, a globally standardized and accepted methodology that also needs to be quick, repeatable and reliable, have caused a great amount of debate on the efficiency of the analytical methods proposed. Oppositely, the regulatory road operates as a tool to guard the adulteration of high quality, expensive certain products.

The nutrients and the amazing flavor of the extra virgin olive oil (EVOO) make it highly requested and has been given the best grade among all types of olive oil, in comparison with other edible oils. Except for the nutritional value, EVOO has an important economic value. Consequently, the adulteration by adding lower-quality oils (refined olive oil, refined olive pomace oil, etc.) is commonly used, and there is a need for its fast and proper noticing [1-3]. The vibrational spectroscopy signatures combined with pattern recognition analysis is one the most contemporarily introduced ways as for a non-catastrophic method for verifying the EVOO [4]. Commercial EVOO samples have been tested and targeted in making predicting models for continuous checking of the olive oil quality parameters to accomplish a fast perceptible analysis for auditing the criteria of the oil quality. Finally, this work concluded that there is a call for applicable, deduced information of adulterating.

Extra virgin olive oils are more valuable than other oils, yet they seem to have related physical characteristics, thence lessening the possibilities of identifying mixtures through an analysis of important ingredients. In some cases, highly adulterated extra virgin oil that doesn't meet the extra virgin requirements, is appeared as EVOO in the market. It is also worth mentioning that a big number of reports have been noted when the International Olive Council applied legal criteria for the spotting of deceitful activity [5,6].

Regarding the background (variety, origin) of the virgin oil, there is a difference in the relative identification, that has been separated in three strategies: the first is the profiling application usage, or targeted analyses. Second is the utilization of the untargeted ones. The last strategy hints the practice of fingerprinting ways that use a chemometric screening of the entire sample fingerprint to recognize key markers that are distinct in the place of formation and/or varieties of interest. No matter which approach is used, chemometric models that are made by the usage of dissimilar multivariate data analysis have been in use to receive a proper distribution of the variety and/or geographical roots of the samples.

Worse oils could have more alteration that can cut out much of the preferable taste-related features that are gotten by an extra virgin oil [7]. Adulterating is usually the inclusion and/or the swapping of lower quality and edible oils [6]. In [6], EVOO standards failed because of: "(a) oxidation by exposure to elevated temperatures, light, and/or aging, (b) adulteration with cheaper refined olive oil, and (c) poor quality oil made from damaged and overripe olive processing flaws, and/or improper oil storage".

Mossoba et al. [8], studied the effects of the contents of three possible adulterants fatty acids on the potential of FT-NIR spectral methodology, simultaneously with partial least squares to fast find EVOO verification, possibly mixed with refined olive oil (RO) or other oils of lower quality. The study was strictly established on whether the components of the fatty acid were within the allowable established ranges. Their findings were consistent with sensory panels; therefore, it indicated the accuracy of the composition of the recognition of the adulterer olive oils as well as and the market's views. Kanavouras el al. [9] agreeing with the approach mentioned before, made an optimal group of taste compounds that have been said to be quality indices of EVOO, when packed and stored in several conditions and with plethora of materials. The researchers, after including in models these compounds, they were able to forecast the shelf life of each olive oil sample, signifying that these flavor compounds can be used as markers for the identification of the source of the oxidative degradation of the olive oil, according to its "storage history".

Kanavouras and Coutelieris [10], have used this model to investigate the shelf life of packaged olive oil, in 2 years' time with plenty of light, temperature and temperature conditions on the storing. This way they could picture the "real-life" situations. This work emphatically reaffirmed the unfavorable role of uncovering additional virgin olive oil to light for more limited or longer periods, since it could fundamentally stimulate the oxidative corruption caused by raised temperatures and presence of oxygen. Besides, plastic, versus glass, was additionally considered as a defensive packaging material for EVOOs.

Furthermore, Coutelieris and Kanavouras [11] utilized a set of mass transport equations for depicting the substance responses that take place in the oil phase, along with the diffusion of oxygen in the oil phase and through the packaging material. The above set was numerically integrated for different combinations of temperatures, light conditions, and packaging materials. The work resulted that the recommended model could be utilized as a tool for a precise forecast of the quality issues for bundled olive oil. In addition, blending olive oils of various geographical and varietal origins is one more subject of concern [12].

Given the cost of the instruments, which often are not accessible for many olive oil laboratories, it is assumed that they will not become an alternative to conventional methods in a short-term scenario. It appears to be important to consider further improvements which should target working on the representativeness of the examined tests to the principal olive-developing regions and developed assortments along with the work of savvy analytical strategies.

A significant worry in giving a reliable approach has been the exact and tedious techniques proposed, of problematic precision, reproducibility, and standardization [13]. Analytical science has prompted the advancement of contemporary scientific instruments that permit the extraction of lot of compound data for an enormous number of tests somewhat rapidly and easy. Nonetheless, the created scientific information (spectroscopic, chromatographic, isotopic, sensorial, and so forth) are frequently multivariate information networks which request proper chemometric examination. In chemometrics, numerical and measurable strategies are utilized for handling and catching the most significant and important content inside the multivariate information [14].

There is also an expanding interest for the presentation of novel and more canny example recognition strategies for handling more perplexing foods [15]. The conventional chromatographic methods recognize the olive oil adulteration dependent on some marker mixtures (triacylglycerols, unsaturated fats, sterols, unsaturated fat methyl esters, etc.). Notwithstanding, these strategies are tedious and includes complex labor-intensive sample preparation for extraction of marker parts from oil tests, while additionally display antagonistic effects on the climate because of the great utilization of unsafe synthetics (plastics). Thus, scientists are ceaselessly engaged to foster fast, precise and environmental-friendly methods for the recognition and quantification of EVOO adulteration.

Besides, this adulteration research has been condemned for its capacity to distinguish the nature of added adulterants. Another shortcoming has been encountered in recognizing low level adulteration, in distinguishing certain debasements, in checking olive oils labeled with geographic indications or certified as monovarietal olive oils. Subsequently, the work to improve the previously mentioned impediments and troubles is continuous, alongside the innovative advances and the analytical processes [16, 17].

The models are identified with the quantification of certain chemical groups and the pertinent synthesis in olive oil, while when coming to quality, some parameters are not considered by all the checked-on olive oil norms exchanges [18]. Then again, it has likewise been recommended that an optimal chemical procedure might be further developed when new methods and new devices will be overhauled, like those based on the vibrational spectroscopy, digital imaging and so on.

The time and resources needed for these examinations regularly mean they can't be effortlessly finished by customs on location or organizations inhouse, and tests should be shipped off licensed testing research centers to be investigated. With the increment of worldwide olive oil imports, particularly in nations where olive oil is a moderately new item to purchasers with less experience and information [19], there is a pressing interest for a a time-efficient and cost-effective adulteration detection for work with or supplant the conventional olive oil virtue examinations. Thus, a requirement for a reliable "confirmation" procedure, dependent on strong enactment, analytical techniques, grounded quality and immaculateness parameters and thresholds within the norms and guidelines is, from an expansive perspective, the idea of controlling fake practices, like contaminated, mislabeling, and deceiving beginning, among others [20].

This work presents a model-based methodology for assessing potential adulteration of EVOOs. The novelty of this approach is justified by the limited use of models in estimating compositional changes of olive oil in close relationship to the supply chain environment and the packaging factors. Consequently, the proposed model is pointing in correspond the assessed timeframe of realistic usability to the initial composition of olive oil, when bottled. As far as shelf life is strongly depended on the storage parameters (temperature, light and packaging materials), these parameters should be considered in that model, as well. Specifically, the flavor profile is comprehensively considered as a marker of product's shelf-life. All in all, this work suggests that since changes in olive oil's compositions affect its shelf life, then it is these deviations from the preferred shelf life of extra virgin olive oils that shall indicate the compositional changes, provided that packaging and storage (supply chain) conditions are remaining the same..

2. Materials and Methods

2.1. Theory

Oxidation of bottled olive-oil is initiated and progresses due to the oxygen entering the bottle and transported within the oil phase, and light that is the photo-oxidation initiator. Both phenomena can be controlled by the permeability of packaging material and its light transparency via the materials' color that may allow a certain fraction of light to pass in the oil or not at all. Although many reactions take place simultaneously during olive-oil oxidation, it is widely accepted that it can be described through the following chemical reaction expressions [21].

$$O_2 \xrightarrow{k_a, h_v} O_3^- \qquad \text{(1a)}$$

$$RH + O_3^- \xrightarrow{k_b} ROOH \qquad \text{(1b)}$$

$$RH + O_2 \xrightarrow{k_C} ROOH \qquad \text{(2)}$$

where k_a, k_b and k_c are the temperature dependent reaction rate constants, mathematically estimated through experimental results, elsewhere [9]. From the mass transport point of view, the oxidation process is as follows: Initially, oxygen penetrates the potentially permeable packaging material, which is a diffusion driven process [22] while the controlling parameters are the permeability of the packaging material and the environmental temperature. After entering the oil, oxygen is diffused and, at the same time, reacts with the oil phase's components. Several flavour compounds are produced which are also diffused in the oil to produce a homogeneous mixture. Among those outcomes, it is hexanal that is widely accepted as the most representative measurable one, which may then actually reflect the quality of bottled olive-oil [23]. Moreover, during the photo-oxidation process, photoexitised oxygen molecules are transformed to active oxygen ions in the presence of light, while these ions react with the existing hyperoxides to produce flavour compounds, as well. The whole process has been described in terms of mathematics (transport equations) elsewhere [24].

Consequently, we may safely assume that having obtained the evolution of the hexanal concentration, we are able to estimate the possibility of the olive-oil to reach the end of its shelf-life, P_{safe}, as follows:

- Initially we define a threshold for the lowest highest acceptable concentration
- We calculate the area between the concentration curve and the threshold line
- We calculate the whole area under the concentration curve
- We divide the above two areas

This ratio represents the possibility of the concentration to overcome the threshold, thus the possibility for the product not to reach the end of its shelf-life. That is logic, considering that the area described in the nominator represents the accumulation of all the unacceptable values of product's quality index (i.e. concentration of hexanal). Finally, P_{safe} equals to unity minus this ratio. The above procedure is mathematically described as follows [10]:

$$P_{safe} = 1 - \frac{\int_{t_{cr}}^{12} \langle C_{hexanal}(t) \rangle dt}{\int_{0}^{12} \langle C_{hexanal}(t) \rangle dt} \quad (3)$$

where, a time interval of 12 months has been arbitrarily defined as the evaluation period. In addition to the concentration profile, the application of the above formula presumes also the knowledge of the critical time, t_{cr}, which is the value of time when the threshold line intersects the concentration curve. The estimation of this value can be obtained only numerically (see, for instance [11]).

A significant part of the simulation described above, is the integration of the mass-transport differential equations, both in oil and packaging phases. To achieve such an integration, it is necessary to superinduce initial and boundary conditions, as described in detail in [24]. Among them, the most important is the amount of hexanal's concentration that initially exists in the oil phase,

$$C_{hexanal}(x \in oil\, phase, t = 0) = C_{hexanal}^{initial} \quad (4)$$

This initial value strongly depicts the composition of the oil before bottling and is supposed to be known experimentally, at least for the case of extra virgin olive-oil [25], which can be used as a reference value. Therefore, a number of cultivational, seasonal, geographical, varietal, extraction process, storage, bottling and conservation supply chain factors, parameters and conditions may as well impact and determine the content of hexanal in a freshly bottled, extra virgin olive oil. Moreover, we may safely assure, that via the improvement-standardization steps of extra virgin olive oil production and distribution, that the amount of initially present hexanal, should remain within a rather narrow range over the seasonal crops production. In this context, any significant variation of this value should correspond to a relative significant variation on the concentration profile and inevitably, impacting the values of critical time t_{cr} and of P_{safe}.

In conclusion, based on the aforementioned physical phenomena within the extra virgin olive oil, any deviation from the initial hexanal concentration corresponds to point in time that product's quality is lower than an acceptable limit, which differs from the relative value for the extra virgin olive-oil. In other words, different values of product's life reflect different initial compositions of the oil-phase, thus could safely indicate adulterations of the product before its bottling.

The concentration values for hexanal used here were previously published in [9], where the shelf life of bottled extra virgin olive oil has been experimentally obtained. For the purposes of present work, it is adequate to compare the P_{safe} values among known extra virgin olive oil samples and samples in question for adulteration. It is needed to stress out that no samples of olive oil were adulted, yet, any potential adulteration were theoretically conceived for the sake of comparisons. In other words, we assumed that hexanal concentration proceeds according to olive oil initial composition. Therefore, the purpose is to present potential deviation from extra virgin olive oil rather than to identify the adulteration itself. This is a reverse-engineering approach, where one may avoid chemical analyses of the sample in question just after the bottling by alternatively simply using the P_{safe} approach. This is possible, since the P_{safe} approach is definitely correlated to the shelf life of olive oil via the time at which the quality indicator, i.e. the hexanal concentration evolution in time, is surpasses the pre-defined quality threshold limit. In the present study, where the quality indicators of extra virgin olive oil at the time of bottling are known, and the t_{cr} and P_{safe} values are estimated for the particular extra virgin olive oil, what is of interest is the weighted deviation of the calculated P_{safe} values from those of the non-altered one. Therefore, the methodology and the outcomes are focusing on this aspect. Actually, the outcomes are presented quantitatively on the base of the absolute difference of the observed P_{safe} values between the normal and adultered olive oil, weighted (divided) by the reference ("normal") P_{safe} value.

2.2. Simulations

Following the analysis presented in [24], the equations were solved by using numerical approaches. Apparently, this integration has evolved the initial conditions and the boundary ones while the appropriate parameters' values have been estimated, as well. Furthermore, the hexanal concentration profiles have been used to estimate t_{cr} and, consequently, P_{safe} for a great variety of storage cases. Especially for the initial condition given in the above eq. (4), we have considered a variation range from -50% to +50%, with respect to the experimentally obtained value of the flavour initial concentration for the case of extra virgin olive oil. A multivariate step of increment in this range was used, being denser for adulterations close to the "normal" olive oil and becoming sparser at the edges of the concentration's interval. Two different representative packaging materials (PET, Glass) have been considered, as well. For their physical and chemical properties see [24]. Regarding the storage conditions, we have assumed (a) three constant temperatures (15^{o}C, 30^{o}C, 40^{o}C) under continuous dark, (b) the same temperatures under continuous light, and (c) a number of various scenarios, (Table 1), as also presented in [10]. The numerical methods applied were as described in [24].

Table 1. Summary of the various combined storage conditions.

Name	Light/Dark	Temperature	Remarks
1A	Continuous Dark	Various	4 months = 15 ^{o}C, next 4 months = 30 ^{o}C, next 4 months = 40 ^{o}C
1B	Continuous Light	Various	4 months = 15 ^{o}C, next 4 months = 30 ^{o}C, next 4 months = 40 ^{o}C
2A	Various	Constant 15 ^{o}C	12 hours dark-12 hours light every day for 12 months

2B	Various	Constant 30 ^{o}C	12 hours dark-12 hours light every day for 12 months
2C	Various	Constant 40 ^{o}C	12 hours dark-12 hours light every day for 12 months
3A	Various	Constant 40 ^{o}C	Continuous dark for 1 month and 12 hours dark-12 hours light every day for next 11 months
3B	Various	Constant 40 ^{o}C	Continuous dark for 2 months and 12 hours dark-12 hours light every day for next 10 months
3C	Various	Constant 40 ^{o}C	Continuous dark for 3 months and 12 hours dark-12 hours light every day for next 10 months
4	Various	Various	

3. Results & Discussion

Having solved the set of differential equations defined in the model, it has been able to produce hexanal concentration profiles for the predefined time period of 12 months. For the sake of demonstration and space economy, the following Figure 1 depicts indicative hexanal concentration profiles for one storage case scenario: PET, constant temperature 30^{o}C and continuous light. Each line corresponds to the evolution of hexanal for different initial concentration in oil-phase, namely, varying ±50% from the experimentally measured value for extra virgin olive-oil (“Normal”). The concentration profile increases sharply at the initial period of storage, attaining a plateau at the later stages due to the extinction of the highly reactive fatty acids, that are the oxidation susceptibility factors. It is rather clear here that the concentration profiles’ shape is highly alike with each other, indicating that the shape is mainly defined by the transport mechanisms themselves rather than the initial hexanal concentration values. On the other hand, the values that hexanal concentration attains depend on the initial values, i.e. higher initial hexanal concentrations conclude to higher consecutive concentrations for the given time period, as presented herein. This outcome allows a quite safe use of the model, independent of the extra virgin olive oil used, since the evolution of the initial hexanal concentration is apparently dependent on the olive samples (different values defined by eq. (4)) providing an adequate identification of different samples.

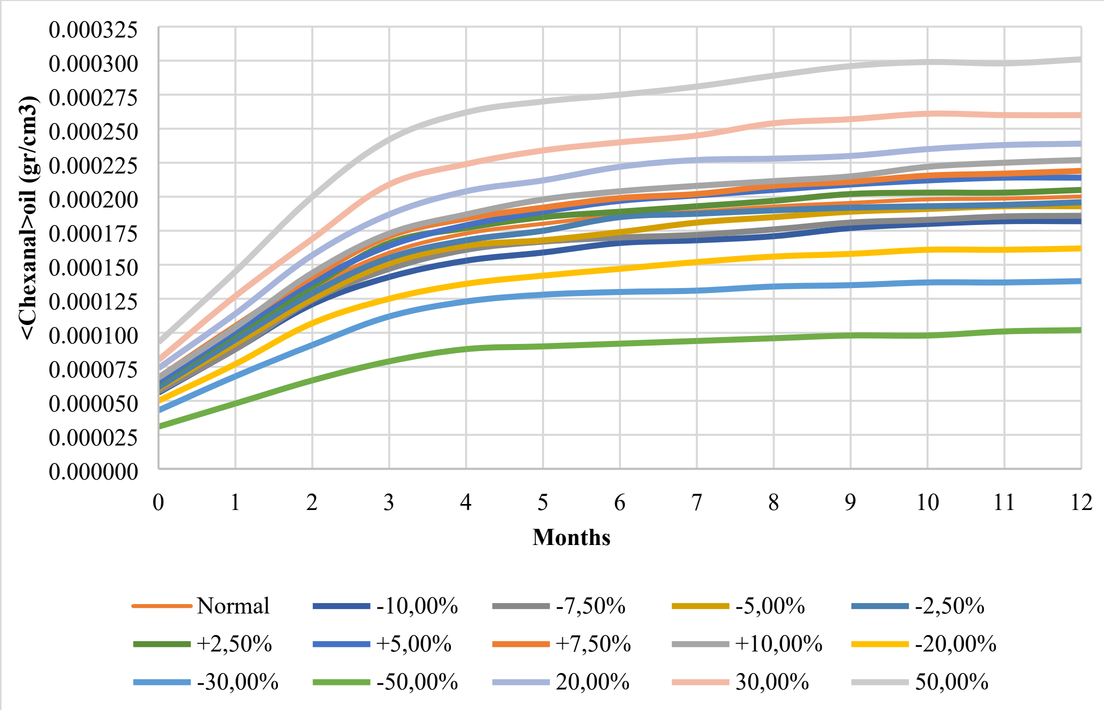

Figure 1: Indicative hexanal concentration profiles as a function of initial values of these concentrations for specific packaging material and storage conditions (PET, 30°C, continuous light exposure).

As presented in eq. (3) and the relevant discussion, different concentration profiles correspond to different P_{safe} values for a given constant threshold.

The following Figure 2 depicts the weighted deviation of P_{safe} values from the extra virgin olive oil ones. The P_{safe} has been estimated by using a standard constant threshold, defined as the upper most level of acceptable hexanal concentration in the olive oil. The value of the threshold was set to be 20% higher than the initial value of hexanal in the extra virgin olive oil at the time of bottling. This value has been kept constant for all the cases presented in this work due to fact that any sample of olive oil under investigation cannot be known at that time as adultered or not, nor at with level. These aforementioned deviations presented for PET and glass packaging materials and for the temperatures of 15°C, 30°C and 40°C, as well as for light and/or dark exposure. The exposure to temperature and light/dark conditions are taken to be constant for 12 months period.

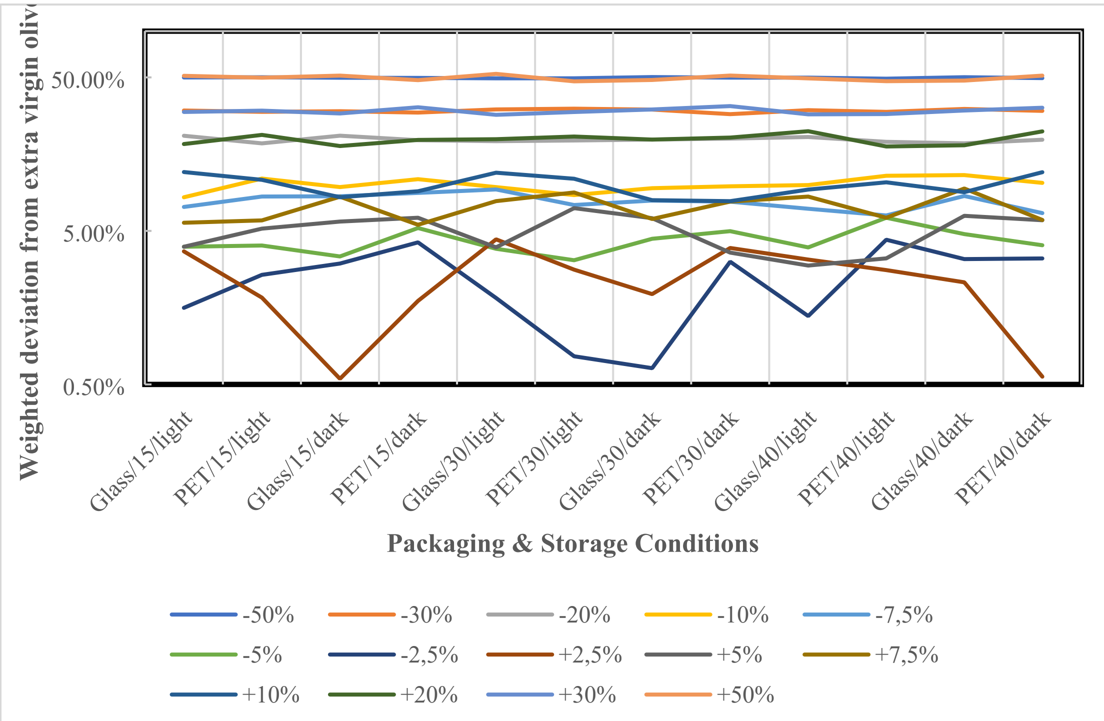

Figure 2: Weighted deviation of P_{safe} values from the extra virgin olive oil ones for various packaging materials exposed at continuous storage conditions.

As seen in the above figure, the weighted deviation of P_{safe} values from the extra virgin olive oil ones, are strongly depended on the initial oil composition. Furthermore, the greater the deviation from the extra virgin olive oil, the less the impact of packaging and storage conditions on the P_{safe} values. That is clearly apparent due to fact that the curves for those alterations tend to be linear and horizontal, which is not the case at low adulteration levels. In other words, at low adulteration levels the significance of packaging and storage conditions is higher and the weighted deviation of P_{safe} values from the extra virgin olive oil ones is quite diverse signifying the protective role of packaging and the impact of the storage conditions. When extra virgin olive oil is mixed with lower quality olive oils and the substrate for oxidation is highly available and reactive, the production of hexanal is strongly favored for the same amount of oxygen which will now react easily with the low-quality substrate. Therefore, the amount of hexanal concentration will be increased and the P_{safe} will be affected. That phenomenon will proceed as far as the substrate, oxygen and energy (light) are available. These findings strongly indicate the high applicability of this model for the lower level olive oil adulterations in comparison to the high ones, when packaging is considered. This can also be attributed to the consistency of the rest of the parameters integrated in the model (diffusivities in the oil phase and reaction rate constants) that were kept identical to those of extra virgin olive oil. While the effect of elevated temperatures and light have been well known and demonstrated in a number of previous studies, herein, it is also brought into attention for their impact on adultered oils as well.
The applications of the model to various storage cases, as in Table 1, are given in Figure 3. Analogously to Figure 2, the same patterns of weighted deviation from the extra virgin olive oil are reported. Once again, the higher the deviations, the lower the impact of packaging materials and storage conditions. The impact of combined storage conditions is also much clearer for the lower adulteration levels. Although the storage cases were selected based on

particular "real-life" scenarios, they may safely allow us to conclude on the analogous trends for each and every storage case applied. So, the role of storage conditions within a supply chain are also identified via this model and clearly distinguish the adulteration levels.

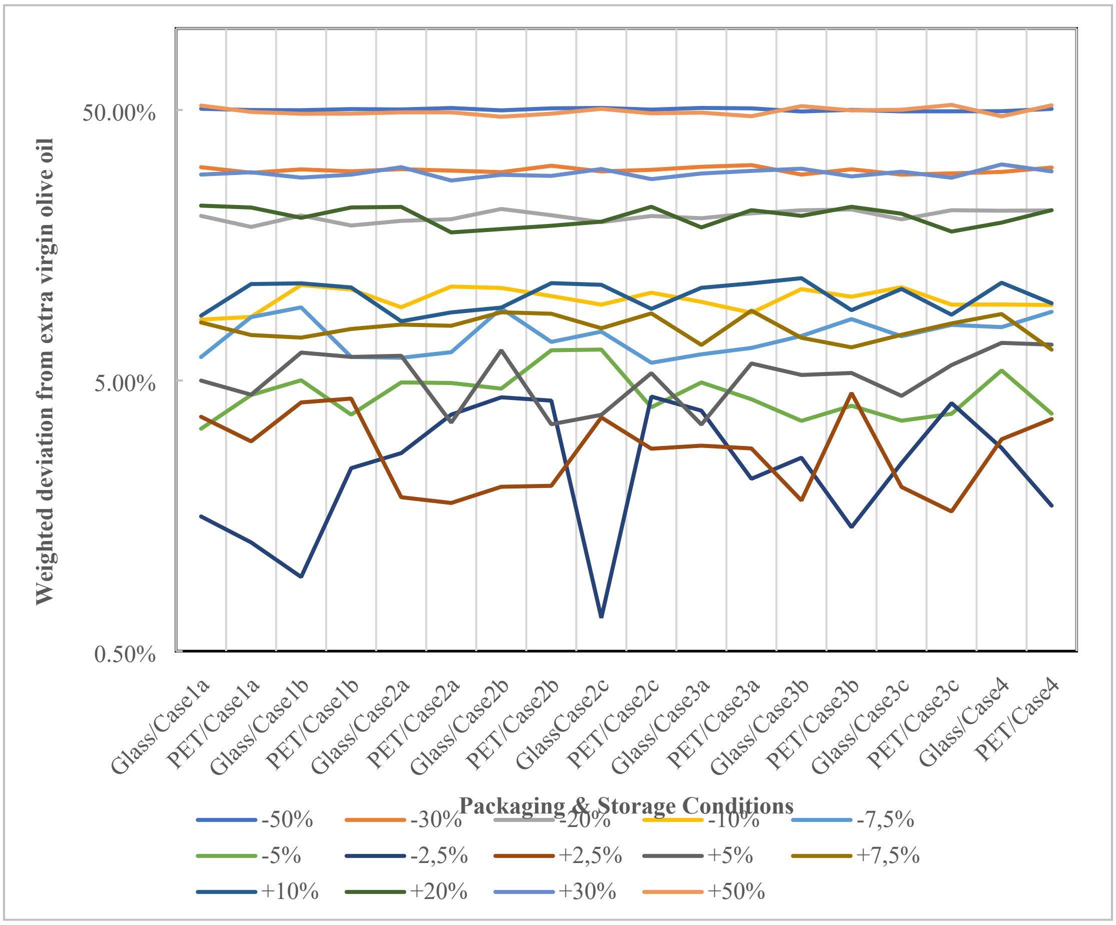

Figure 3: Weighted deviation of P_{safe} values from the extra virgin olive oil ones for various packaging materials exposed at various combined storage conditions, as in Table 1.

4. Conclusions

This work introduces a novel approach, aiming in combining the shelf life with a potential adulteration of extra virgin olive oil with olive oils of lower quality. This combination further considers the packaging and storage conditions as impacting factors to the shelf life. The model applied treats these factors within the shelf life estimations that are used for identifying differences among "normal" and adultered oils. The weighted deviations of P_{safe} values of different levels adultered oils clearly showed the potential of identifying these oils. It is reported that the greater these deviations, the lower the assurance for a pure, non-adultered, olive oil.

This outcome allows for a quite safe use of the model, independent of the extra virgin olive oil used, since the evolution of the initial hexanal concentration is apparently dependent on the olive samples providing an adequate identification of different samples. Moreover, and in alliance to the broadly accepted statistics (intervals of confidence 5%), any deviation higher than 5% may be safely considered as a strong indication of adulteration, thus, a further, detailed and more laborious analysis is highly recommended.

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