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RESEARCH ARTICLE

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FTIR-ATR adulteration study of hempseed oil of different geographic origins

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Abstract

Adulteration of hempseed (H) oil, a well-known health beneficial nutrient, is studied in this work by mixing it with cheap and widely used oils such as rapeseed (R) oil and sesame (Se) and sunflower (Su) oil. Many samples of different geographic origins were taken into account. Binary mixture sets of hempseed oil with these 3 oils (HR, HSe, and HSu) were considered. FTIR spectra of pure oils and their mixtures were recorded, and quantitative analyses were performed using partial least squares regression (PLS) and first-break forward interval PLS methods (FB-FiPLS). The obtained results show that each particular oil can be very successfully quantified (R^2(val) > 0.995, RMSECV 0.9%–2.9%, RMSEP 1.0%–3.2%). This means that FTIR coupled with multivariate methods can rapidly and effectively determine the level of adulteration in the adulterated hempseed oil for these studied and frequently used adulterant oils. Also, the relevant variables selected by FB-FiPLS could be used for verification of hempseed oil adulteration.

KEYWORDS

adulteration, FTIR-ATR, hempseed oil, regression

1 | INTRODUCTION

Adulteration of high-priced edible oils like hempseed oil or olive oil is a serious threat to the industry of edible oils and to consumer's health. Certain analytical methods such as gas chromatography (GC) or liquid chromatography (LC) were found to be useful in establishing the type and level of olive oil adulteration.[1-3] Both macroconstituents (fatty acids as triacylglycerols) and microconstituents (sterols, tocopherols, etc) can be quantified using chromatographic methods.[1,2,4] Other methods were also proposed for detection and quantification of olive oil—using NMR spectroscopy,[5] fluorescence spectroscopy,[6] differential scanning calorimetry (DSC),[7] and mass spectrometry.[8] Most of these previously mentioned methods are time consuming and expensive, and some of them require well-trained analysts.[2]

Fourier transform infrared spectroscopy (FTIR) in combination with multivariate methods has been established as a very fast and effective tool in classification of adulterated oils, as well as in quantitative prediction of the level of adulteration. Regarding the adulteration of extra-virgin olive oil, this method has been used and described in the literature.[9-14] Olive oil has been tested for adulteration with many cheap adulterants such as sunflower oil, soybean oil, corn oil, palm oil, and rapeseed oil. Except for adulteration of olive oil, FTIR coupled with multivariate methods has also been used for authentication of some other high-priced oils such as coconut oil,[15] camellia oil,[16] and cod liver oil,[17] although these oils are neither produced nor consumed in as high quantities as olive oil. A study of adulteration of vegetable edible oils was conducted even with oils used for frying.[18] In addition to FTIR spectroscopy, UV-Vis

spectroscopy,[19] NIR spectroscopy,[20] and Raman spectrospopy[21] in combination with multivariate methods were also utilized for authentication of vegetable oils and fats.

Our previous work used 1 pure hempseed (H) oil sample (and its mixtures with adulterant oils) and with focus on the interval ridge regression procedure.[22] Therein, it was bespoken that further studies should consider more samples of different geographic origins. This is what we consider in the current study. The fatty acid composition of hempseed oil corresponds to the ideal ratio of essential fatty acids (EFAs) required by human body, which is roughly 3:1 of omega-6 to omega-3.[23] Hempseed oil also contains γ-linolenic acid, which is important in treatment and prevention of atopic eczema, atopic dermatitis, rheumatic arthritis, alcoholism, cardiovascular disorders, and premenstrual syndrome.[23,24] Due to its significant world production[25] and the mentioned health benefits, it is important to carry out the study on high varieties of both hempseed oils and adulterant oils. In our experiments, hempseed oils will be adulterated with cheaper oils such as rapeseed (R) oil, sesame (Se) oil, and sunflower (Su) oil. Each of the 4 mentioned botanical oils will vary in composition with respect to its geographic origin. Our results obtained in this study denote good prediction models for each considered adulterant in hempseed oil, even when samples from many different geographical origins are taken into account.

Considering the high health benefits, high price, and significant world production of hempseed oil, it is of importance to establish a method for fast and efficient detection and quantification of possible adulterants in this valuable oil. In this work, hempseed oil, due to its high degree of unsaturation, will be adulterated with low priced oils of also relatively high degree of unsaturation, such as rapeseed, sesame, and sunflower oil. The level of adulteration will be determined using FTIR combined with standard PLS procedure and with appropriate variable selection procedure already used in literature—first-break forward interval PLS (FB-FiPLS).[26]

2 | MATERIALS AND METHODS

2.1 | Sample preparation

Commercial oils used in this study were purchased in the city of Zagreb (Croatia). Table 1 represents all 29 vegetable oils used in this study. The samples differ with respect to the botanical origin of the oils: hempseed (15 samples), rapeseed (4 samples), sesame (4 samples), and sunflower oils (6 samples) (Table 1). Each botanical origin of the oils varies with respect to the brand, producer, and geographic origin (ie, in this case, the country of origin, Table 1). Supplementary Table S1 shows more details regarding the composition of each pure oil sample, if it was labeled on the product.

Three binary mixture sets were prepared; HR, HSe, and HSu. There were 60 mixture samples for each of the HR and HSe binary mixture sets and 90 mixture samples for the HSu mixture set. H oil was adulterated with 5%, 10%, 20%, and 30% of R and Se adulterant oils, and with 10%, 20%, 30%, 40%, 50%, and 60% of Su adulterant oil. Because, for example, there were 15 hempseed oil samples and 4 rapeseed oil samples, there were altogether 60 different combinations of binary mixtures with H and R oils. The similar is true for the cases of mixture of H oil with the other 2 adulterant oils. All different combinations were prepared, where each combination had its own adulteration level, as displayed in Supplementary Table S2.

The HR and HSe binary mixture sets therefore comprise 60 binary mixtures and 19 pure oils, while HSu binary mixture set comprises 90 mixture samples and 21 pure oils. The set of all samples contains 239 oils (210 mixture samples and 29 pure oils).

2.2 | ATR spectral measurements

Attenuated total reflectance (ATR) spectra were recorded in the spectral range of 4000 to 600 cm^{-1} with a Bruker Vector 22 spectrometer. The acquisition parameters were 4 cm^{-1} of nominal resolution and 128 scans, thus yielding 1764 spectral variables. The spectrometer was placed in a room with a constant temperature (23°C), and the samples were allowed to equilibrate to the room temperature before measurement.

A single-beam spectrum of the corresponding oil sample was collected and corrected against the corresponding background spectrum of air, so that each spectrum had its own background of the same resolution. One or few oil drops of each particular sample were placed on the diamond ATR crystal, ensuring that no air bubbles were trapped on the crystal's surface. The crystal was cleaned between every 2 consecutive samplings with the Kemex cleaning agent

TABLE 1 Vegetable oil samples used in the adulteration study

Bot. origin[a] (sample no.)	Name-brand/producer or produced for/town	Country of production	Country of origin
H (1)	CannaBio d.o.o., HR-32232 Sotin (Vukovar)	Croatia	Croatia
H (2)	Planet Bio, Kranj	Slovenia	Romania
H (3)	OPZ "TOP", 43000 Bjelovar	Croatia	Croatia
H (4)	Kernnel premium, Myristica d.o.o., 10000 Zagreb	Croatia	Romania
H (5)	Herbio Puls d.o.o., 10410 Velika Gorica,	Croatia	Croatia
H (6)	GEA d.d., Tovarna olja, Sl-2310 Slovenska Bistrica	Slovenia	Slovenia
H (7)	Biosativa d.o.o., 10000 Zagreb	Croatia	Netherlands
H (8)	Nutri oil, d.o.o., 10410 Velika Gorica	Croatia	Croatia
H (9)	Ekozona, 10000 Zagreb	Croatia	Romania
H (10)	Cannabis Pharma, s.r.o., 41501 Teplice	Czech Republic	Canada
H (11)	Encian Bio konopljino ulje, 10250 Lučko	Croatia	Romania
H (12)	Gardenolo, Jan-Spider, 33405 Pitomača	Croatia	Croatia
H (13)	Biorganic, Advent d.o.o., 52100 Pula	Croatia	Canada
H (14)	Sun & Seed Ltd, London	Great Britain	Serbia
H (15)	Garden d.o.o., 10000 Zagreb	Croatia	Romania
R (1)	Alnatura GmbH, 64404 Bickenbach	Germany	France
R (2)	Matičnjak Sativa d.o.o., 10000 Zagreb	Croatia	Croatia
R (3)	Rapunzel Naturkost AG, 87764 Legau	Germany	Germany
R (4)	Basic AG, 81677 München	Germany	Germany
Se (1)	BioGourmet GmbH, 71729 Erdmannhausen	Germany	Germany
Se (2)	Ekoland, Natudis, 3840 AJ Harderwijk	Netherlands	Netherlands
Se (3)	ORGANIC OILS SpA, Mugnano (PG), 06132	Italy	Italy
Se (4)	GEA d.d., Tovarna olja, Sl-2310 Slovenska Bistrica	Slovenia	Slovenia
Su (1)	S Budget, SPAR Hrvatska d.o.o., 10000 Zagreb	Croatia	Hungary
Su (2)	Tena, Tvornica ulja Čepin d.d., 31431 Čepin	Croatia	Croatia
Su (3)	GEA d.d., Tovarna olja, Sl-2310 Slovenska Bistrica	Slovenia	Slovenia
Su (4)	Zvijezda d.d., 10000 Zagreb	Croatia	Croatia
Su (5)	ORGANIC OILS SpA, Mugnano (PG), 06132	Italy	Italy
Su (6)	Davert Muhle, D-48308 Senden	Germany	Germany

[a]Botanical origin of oil.

H, hempseed oil; R, rapeseed oil; Se, sesame oil; Su, sunflower oil.

(Kemika, Croatia), water, and cyclohexane (Merck, >99.5%), and dried. Dry crystal was checked each time for possible remains by applying a few scans.

Each particular sample in all sets was measured twice, except for all samples of pure H oils, which were measured 6 times, thus obtaining altogether 538 spectra. The reproducibility of the recorded spectra was ensured.

3 | MULTIVARIATE DATA ANALYSIS

At first, uninformative spectral wavenumbers containing no vibrational band were removed, so that the whole multivariate analysis was carried out in the spectral region of 3200 to 2600 cm^{-1} and 1900 to 600 cm^{-1} (in further text designated

as the "whole spectral region"). ATR intensities (*y*-axis in Figure 1) of the wavenumbers represent the predictor (independent) variables of the analyzed data sets.

For each of the quantitative prediction methods, the calculations were computed on the whole ATR spectra (predictor variables) of each binary mixture set (HR, HSe, and HSu) and on the set of all samples (ie, altogether 7 different data sets). For each data set, there is a single response variable measuring the volume fractions of each oil sample. Two thirds of the samples were taken for calibration (using LOO CV) and one third for validation. The specifics of evaluation are explained for each quantitative prediction method.

3.1 | Partial least squares regression (PLS)

Partial least squares regression (PLS) is the most often used procedure for quantitative prediction of the adulterated samples. Using the procedure of highest covariance between the matrix of mean centered spectral variables, $\boldsymbol{X}$, and matrix (or a vector) of concentrations, $\boldsymbol{Y}$, one obtains in several steps the vector of regression coefficients, $\boldsymbol{B}$, on the training set, that linearly relates absorbances and concentrations; $\boldsymbol{Y} = \boldsymbol{BX} + \boldsymbol{E}$. By multiplying this vector $\boldsymbol{B}$ with spectra of test samples, one obtains the concentration of interest. Dimensionality of the spectral data is reduced from few thousands of intercorrelated variables to only several completely uncorrelated variables (eg, PLS components) that contain most of the variance present in the data. Due to that, these procedures are established to be very effective in qualitative and quantitative analysis.[27]

PLS calculations were carried out on the ATR spectra of each binary mixture set (HR, HSe, and HSu) and on the set of all samples. PLS was computed on the whole spectral region. The optimal number of LVs used for building the model was determined with minimum RMSECV of leave-one-out (LOO) cross-validation on the calibration set; root mean square error of calibration (RMSEC) was also computed (see Supplementary materials Equations S1–S2). The upper limit of number of LVs was initially set to be 20 in each case. Predictive capabilities were estimated by calculating root mean square error of prediction (RMSEP) (Equation S3) and R^2(val) for the test set (Equation S4).

Mean centering of both spectral variables ($\boldsymbol{X}$) and volume fractions ($\boldsymbol{Y}$) was done before carrying out PLS. Except LOO CV, other forms of cross-validation were also carried out, such as *k*-fold CV (with $k = 10$, 20, 30, and 50), but although slightly higher RMSECV was obtained, RMSEP for the validation set was not significantly changed (when compared with LOO CV) for all 7 cases studied. Thus, we report only the LOO CV results.

3.2 | FB-FiPLS procedure

The RMSECV decreases with increasing number of LVs, but at some point, it increases due to over-fitting. For interval PLS procedures, the upper limit for the number of LVs is critical, because too many LVs enable selection of artifacts in spectra specific for the training set. The PLS model built with the number of LVs in the global minimum of RMSECV generally overestimates the significant number of LVs.[28]

As in our previous work,[26] we employ a modification of interval PLS procedure (FB-FiPLS) as a means to avoid overfitting. Here, the upper limit of LVs was based on repeated double cross-validation (rdCV) procedure performed only on

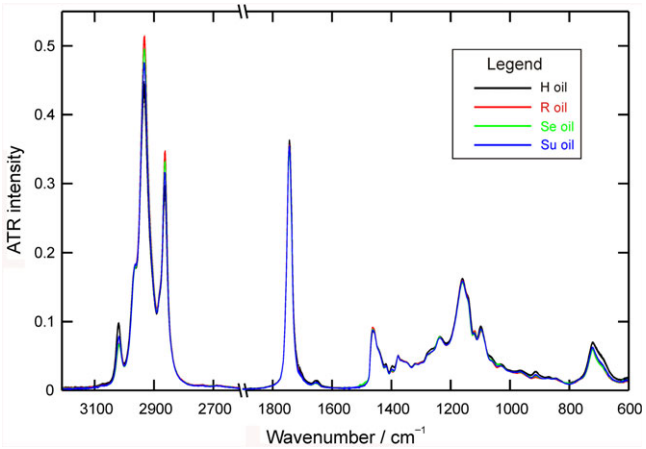

FIGURE 1 ATR spectra (58 spectra) of the whole spectral region for all (29) pure samples of H oil, R oil, Se oil, and Su oil

the whole spectral region; the procedure is explained in detail in Ref. [28], with the same parameters used as in Ref. [26]. In brief, rdCV leads to a conservative estimate for the optimal number of LVs. In rdCV, each segment has its own mean square error (MSE), and because there are more segments in inner loop, there is a mean of MSE and standard deviation of MSE. The smallest number of LVs that are within 2 standard deviations (sdfact = 2) of global minimum of MSE can be selected. The inner loop performs the cross-validation on 10 segments. The number of segments in the outer loop was 4. The optimal number of LVs is based on the highest frequency among all obtained results, in this case 400 obtained results = 4 outer loops × 100 repetitions. In each repetition, random samples are selected for the inner and outer loops.

The wavenumbers were split into equidistant intervals (n_i), numbering from 2 to 50, ie, 49 different n_i. For each n_i, procedure began with the first interval of the lowest RMSECV among all other intervals (using already determined upper limit of the number of LVs). The progress continued in each step by picking that interval, which, when merged with the formerly selected interval(s), yielded lowest possible RMSECV, and it stopped once the RMSECV of the first $k + 1$ selected intervals was higher than k selected intervals. Thus, k selected intervals with the corresponding f number of LVs was the optimal solution for that n_i. After optimal solutions for each n_i had been determined, the final solution was selected according to the lowest RMSECV. For that final solution, n_i with the selected variable intervals and f number of LVs, PLS model was built on a training set with calculated values for RMSEC and RMSECV. That final model was used for fitting the validation set, obtaining RMSEP and R^2(val). The rationale for considering only the first k intervals is that they should contain most chemically relevant information. Thus, a considerable amount of time was saved by neglecting a larger number of intervals.

PLS and FB-FiPLS procedures were performed in program R (R version 3.2.2).[29]

4 | RESULTS AND DISCUSSION

4.1 | Vibrational spectra of the studied oils

ATR spectra of all 29 pure oils are shown in Figure 1. Most of the vibrational bands are already assigned in literature (see Table 2).[22,30] The differences in absorbance of the presented bands between the sampled vegetable oils are visible, even among several spectra of the same botanical origin of oil. Among all botanical oils, hempseed oils have the highest intensity at 3009 cm^{-1}, which belongs to the band of stretching vibration of C—H on olefinic double bonds, which is expected, because hempseed oil has the highest degree of unsaturation. Other subtle differences in ATR intensities can be noticed at 2925 and at 2854 cm^{-1}, which are the bands of antisymmetric and symmetric stretching vibration of methylene and methyl groups, while the band at 723 cm^{-1} is assigned to both CH_2 rocking and bending of *cis*-disubstituted olefins. In the fingerprint region, note both bending vibrations of aliphatic and olefinic functional groups and C—O stretching vibrations (Table 2).

4.2 | Quantitative determination of adulteration

Final results of PLS and FB-FiPLS are displayed in Tables 3 and 4, respectively. On average, FB-FiPLS attained slightly lower RMSEP than PLS, and in 3 out of 7 cases, the difference is significant ($P < 0.05$) (Table S3). Besides RMSEP, FB-FiPLS selected much less variables with lower number of latent variables for optimal prediction models. The results shown are for LOO cross-validation. In addition, there was no significant difference between LOO and k-fold cross-validation.

Based on sample labels, hempseed oil samples varied mostly in polyunsaturated fats (73%–78%) and omega-3 fatty acids (16%–20%). Adulterant oils varied in monounsaturated fats (R oil 57%–62%, Se oil 36%–40%, Su oil 24%–31%) and polyunsaturated fats (R oil 25%–31%, Se oil 40%–45%, Su oil 59%–67%) (Table S1). Despite that, attained RMSEP for binary mixtures is satisfactory (RMSEP in range 1.0–3.2) and very similar to that obtained for the adulteration of extra-virgin olive oil with sunflower in literature, concerning slightly lower number of samples (RMSEP = 2.1).[31] Similar is also true regarding R^2 values.[32] Using HPLC data with interval PLS for models with many samples of vegetable oils, attained RMSEP in literature is even ≈10%,[4] while in this work it is 1.0%–3.8%. PLS models on FTIR data of more samples of extra-virgin olive oil and many more different adulterant oils (altogether 111 pure oil samples) were also considered in literature, but that resulted, at best, only in rough predictive capabilities (RMSECV = 8.3%).[11]

Reproducibility was assessed as the standard deviation (see Supplementary Equation S5 and below) of both cross-validated predicted values of the training samples and the predicted values of the test samples. With FB-FiPLS, the

TABLE 2 Assignment of vibrational bands of edible oils reported up to date[22,30]

ν/cm^{-1}	Band assignment
3008	Stretching of C—H on *cis* C=C bond
2962	Antisymmetric stretching of C—H in CH_3
2925	Antisymmetric stretching of C—H in CH_2
2872	Symmetric stretching of C—H in CH_3
2854	Symmetric stretching of C—H in CH_2
1746	Stretching of C=O in COOR
1711	Stretching of C=O in COOH
1654	Stretching of *cis*-C=C
1465	Scissoring of C—H in CH_2 and CH_3
1418	Rocking of C—H on *cis* C=C bond
1397	Bending of C—H on *cis* C=C bond
1377	Bending of C—H on CH_2 and CH_3
1238	Stretching of C—O in COOR
1163	Stretching of C—O in COOR, bending of C—H on CH_2
1118	Stretching of C—O
1097	Stretching of C—O
1068	C—O and bending *cis*-HC=CH of linolenic acid
1033	Stretching of C—O
968	Bending out of plane of *trans*-HC=CH
914	Bending out of plane of *cis*-HC=CH
723	Rocking of CH_2 and out of plane bending of *cis*-disubstituted olefins

TABLE 3 Detailed results of PLS, the maximum of 20 LVs for all considered sets

	No. of variables	*f*(LV)	RMSECV/%	RMSEC/%	R^2(train)	RMSEP/%	R^2(test)
R (bin.)	988	8	1.3995	0.7110	0.9990	1.4406	0.9959
Se (bin.)	988	9	2.2262	0.8794	0.9985	2.3230	0.9909
Su (bin.)	988	10	3.2322	1.2885	0.9976	3.1346	0.9848
H (all samp.)	988	11	3.4452	2.6379	0.9889	3.3151	0.9836
R (all samp.)	988	15	1.5129	0.8396	0.9966	1.6765	0.9873
Se (all samp.)	988	13	2.2604	1.4113	0.9912	1.9539	0.9775
Su (all samp.)	988	14	4.1606	2.4421	0.9893	3.4381	0.9782

attained reproducibility for the binary mixture sets is as follows: 0.687% for R in HR, 0.767% for Se in HSe, and 1.280% for Su in HSu.

If only a single pure sample of Su oil was used to adulterate only a single pure sample of H oil, a lower RMSEP (of ≈0.6%) would be attained,[22] but not much lower in the case of 1-sample adulteration of R oil (≈0.9%).[22] Therefore, the presented results show that even if many samples and sample mixtures with high variation of geographic origin concerning both adulterant oil(s) and hempseed oil are taken into account, the quantitative predictions of each component are accurate.

The analysis of optimally selected wavenumbers using FB-FiPLS can be seen below Table 4. Bolded part of selected ranges depicts first selected interval, which denotes the most important spectral range.[26] For R in all

TABLE 4 Detailed results of FB-FiPLS, the maximum of 20 LVs for all considered sets

	No. of variables	*f*(LV)	RMSECV/%	RMSEC/%	R^2(train)	RMSEP/%	R^2(test)
R (bin.)	217[a]	7	0.8825	0.6477	0.9991	1.0018*	0.9981
Se (bin.)	102[b]	4	1.7912	1.6941	0.9940	1.9271	0.9930
Su (bin.)	276[c]	5	2.9161	2.7201	0.9887	3.2205	0.9836
H (all samp.)	252[d]	6	3.3242	3.1583	0.9839	3.4522	0.9813
R (all samp.)	278[e]	9	1.2312	1.1195	0.9938	1.4179*	0.9910
Se (all samp.)	242[f]	6	1.9435	1.8169	0.9852	1.6702*	0.9836
Su (all samp.)	147[g]	7	3.8175	3.6232	0.9760	3.8153	0.9730

*Statistically significant difference ($P < 0.05$) between PLS and FB-FiPLS concerning either the paired *t*-test or the *F*-test (Table S3).

Selected variables:

[a]1886–1849, 1462–1348, 1308–1232, **1115–1039**, 1001–930, 854–820 cm^{-1}.

[b]1450–1387, **1122–1059**, 926–862 cm^{-1}.

[c]3113–3070, 2625–2602, 1901–1884, 1749–1662, 1483–1308, **1128–1041**, 951–908, 862–820 cm^{-1}.

[d]3078–3039, 2916–2877, 2713–2675, 2632–2602, 1901–1896, 1448–1369, 1286–1248, **1124–1086**, 962–883, 760–681 cm^{-1}.

[e]1716–1672, 1577–1533, 1441–1398, 1352–1221, **1130–1043**, 997–910, 864–822, 775–733 cm^{-1}.

[f]1616–1533, **1489–1406**, 1361–1236, 1149–1066, 937–897, 810–769 cm^{-1}.

[g]1408–1369, 1286–1248, **1124–1045**, 1003–924, 760–721 cm^{-1}.

samples, the most important selected intervals are those that account for the C—O stretching vibrations and linolenic acid at 1068 cm^{-1}; also important is out-of-plane bending vibration of *cis*-HC═CH. For Se in all samples, the most important interval is 1489 to 1406 cm^{-1}. It is known that sesame oil has a relatively high amount of unsaponifiable matter relative to the other oils and that it contains a high amount of very specific lignans such as sesamin.[33] IR spectrum in literature for sesamin shows very strong bands at approximately 1500, 1489, and 1444 cm^{-1}.[34] The bands are weak in intensity but can be seen in IR spectra of pure sesame oils, and the selected most important interval corresponds with these bands for sesamin. For sunflower oil, the most important variables are the C—O stretching vibrations and the vibration for linolenic acid at 1068 cm^{-1}.[35] These selected variables could be used for verification of hempseed oil adulteration.

5 | CONCLUSION

In this study, for the first time, many different samples of hempseed oil were used for establishing quantitative prediction models for assessing adulteration with adulterant oils. The type and level of hempseed oil adulteration can be accurately determined for each considered binary mixture (RMSECV 0.9%–2.9%, RMSEP 1.0%–3.2%), despite the varying origin of considered samples and their content from many different European countries and some samples from outside of Europe.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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