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Use of X-ray diffraction technique and chemometrics to aid soil sampling strategies in traceability studies

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ABSTRACT

Aim of this work is to assess the potentialities of the X-ray powder diffraction technique as fingerprinting technique, i.e. as a preliminary tool to assess soil samples variability, in terms of geochemical features, in the context of food geographical traceability. A correct approach to sampling procedure is always a critical issue in scientific investigation. In particular, in food geographical traceability studies, where the cause–effect relations between the soil of origin and the final foodstuff is sought, a representative sampling of the territory under investigation is certainly an imperative. This research concerns a pilot study to investigate the field homogeneity with respect to both field extension and sampling depth, taking also into account the seasonal variability. Four Lambrusco production sites of the Modena district were considered. The X-Ray diffraction spectra, collected on the powder of each soil sample, were treated as fingerprint profiles to be deciphered by multivariate and multi-way data analysis, namely PCA and PARAFAC. The differentiation pattern observed in soil samples, as obtained by this fast and non-destructive analytical approach, well matches with the results obtained by characterization with other costly analytical techniques, such as ICP/MS, GFAAS, FAAS, etc. Thus, the proposed approach furnishes a rational basis to reduce the number of soil samples to be collected for further analytical characterization, i.e. metals content, isotopic ratio of radiogenic element, etc., while maintaining an exhaustive description of the investigated production areas.

1. Introduction

Nowadays, there is a growing attention among consumers for high quality food with a clear regional identity. Consequently it is increasing the need to identify frauds, such as commercialization of fake or sound-like products. The association between food quality and territoriality is a well-accepted assumption (cf. EC regulations 2081/92 and 1898/06) in the European Community and many producers have chosen to stress the product territoriality as a quality indicator in order to emphasize their marketing strategies. Thus, the possibility to establish objective criteria to trace the origin of food and to follow its production process is critical to guarantee not only the consumers, but also the producers, in order to promote high levels of safety, hygiene and to protect their products. This is especially true as regards traditional food excellences, awarded with origin labels such as PDO (Protected Designation of Origin), PGI (Protected Geographical Indication), etc., whose certification of authenticity is at present mainly paper based and thus easy to be falsified.

In this context, it is raising the number of researches [1–4] and research projects [5,6] regarding the improvement of efficiency in food chain and the tools for traceability of the production processes. Moreover, great attention is paid to the use of metals composition and isotopic ratios as primary origin indicators, namely able to give account of the direct cause–effect relationship between soil of origin and food. In order to build reliable geographical traceability models based on these analytical approaches, some major issues have to be taken into account. Primarily, it is necessary to accurately plan the sampling of all the involved matrices, from soil to finished food, because this is determinant for the meaningfulness of the final results. As second point, an evaluation of the role of the bioavailability of the specimen in the plant uptake process through the final product must also be assessed to have a more defined picture of the overall potentialities of these markers.

As regard to soil, several strategies have been proposed to plan a representative sampling [7,8], such as the use of regular and circular grids, systematic and non-systematic patterns, and unaligned random sampling. These approaches are generally aimed at uniformly sampling the investigated area, taking into account only few variables, in most cases the geographical coordinates. However geographical markers result to be highly affected by the

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geochemistry, and thus by the nature and composition of soils, which can greatly vary both inter- and intra-sites and also along the vertical profile [9,10]. Therefore, the investigation of the homogeneity of soil results to be particularly important in order to choose location and depth of samples to be collected.

The measurement of the above mentioned indicators, metals and isotopic ratios, require complex procedures [11–13], which are expensive and time consuming. First of all, a suitable extraction or digestion of the samples is required [9]. Moreover, in the isotopic ratio determination, other treatments, such as resin separation, are needed in order to remove isobaric interferences [13,14]. For these reasons, it is not feasible to fully characterize the whole investigated area through the determination of such indicators. Thus, it would be useful to find out a screening methodology for the assessment of the influence of sampling depth, field homogeneity, seasonal and time variability, in order to finally plan a reasonable and affordable number of soil samples to be collected, where these indicators have to be determined. In this work, the use of X-ray diffraction of powder is suggested as a technique suitable to implement a blind analysis approach on soil samples, because it provides simple and relatively fast determinations, producing a fingerprint, which could be related to the different composition and morphological structure of the soils. Hence, X-ray diffractograms were treated in a non-conventional way, merely analyzing the signals as a whole by means of chemometrics techniques. This approach permits to point out the similarities and differences among soil samples without the need of identifying and quantifying a priori the amorphous and crystalline components that characterize them. The work herein reported is a part of a food traceability project founded by the AGER platform [6] concerning enological products. The long term aim of this research program is to assess geographical traceability models for the worldwide known PDO enological products of the Modena and Trento districts, such as the Lambrusco and Trentodoc wines. In this context, the ability of the proposed screening technique in investigating the field homogeneity, sampling depth influence and seasonal and time variability of the territorial variables is studied.

2. Experimental

2.1. Soil sampling

The enological products, object of this work, are subjected to stringent regulations [15,16] that allow the grapes cultivation in the whole Modena district. The first step for the achievement of significant geographical traceability models is the full characterization of the territory of origin. The province of Modena is located in the north of Italy and the territory spans an in-plain area, centre–north area, and a moderate/medium hill in the southern part. Moreover, the northern left and right boundaries are comprised of the Po, Secchia and Panaro rivers whose alluvial basins have a deep influence on the pedo and lithological characteristics of the territory. Owing to the large area that has to be sampled (4062 producers, 90 km^2 of cultivated fields) and to the peculiarities of the different places, a pilot study has been started in order to evaluate, on a reduced scale, the sampling conditions and procedures. For these reasons, the attention was focused on four farms that include the whole production chain from the raw materials to the final products and are representative of the investigated area; three of these (producers A, B and D) are located in an in-plain region, whilst the other one, producer C, is located in hill area. Three to five soil samples were collected within each field, Table 1A (available as Supplementary materials), using a manual percussion single gauge auger (3 cm internal diameter) set for hardly disturbed samples. This tool allowed sampling 5 soil aliquots, starting from a depth of 10 cm up to 60 cm (a=10–20 cm, b=20–30 cm, c=30–40 cm, d=40–50 cm, e=50–60 cm). The deepest value corresponds to a depth where more than half of the grapevine root system is developed [17]; the upper 10 cm (0–10 cm) were removed because of the possible presence of grass or superficial debris.

The sampling procedure was repeated in three different period of the year, namely: spring 2009, summer 2009 and winter 2009/2010, in order to evaluate the seasonal variability related both to the weather conditions and/or to the occurred vineyard treatments. In this way the total number of analyzed samples was 240, namely 16 sampling sites $\times$ 5 depths $\times$ 3 seasons.

In order to collect the X-ray diffraction spectra, the soil samples have to be homogenized and reduced to powder form. Therefore, all the samples were minced using a Teflon spatula and then dried at 100 ± 2 °C in an oven for 24 h. After that, the soils were ground by using a centrifugal mill to a 250 μm particle size and finally stored in hermetic polystyrene containers.

2.2. Instrumentations

An ISCO oven, model MPC3, was used to dry all the soil samples.

A Fritsch variable speed centrifugal mill, model PULVERISETTE 14, equipped with: pure Titan 12 ribs rotor, 250 μm trapezoidal titanium sieve ring and Teflon coated collection pan, was used to grind the samples.

X-ray diffraction of powder, XRDP, was carried out by a θ/θ PANalytical X'Pert Powder diffractometer equipped with a Real Time Multiple Strip (RTMS) detector (PANalytical X'Celerator). A 0.5° divergence slit and a 0.5° anti-scatter slit as well as a soller slit (0.04 rad) and a 10 mm mask were mounted along the incident beam pathway. The diffracted beam pathway included a Ni filter, a soller slit (0.04 rad) and an anti-scatter slit (5 mm). The XRD data were collected from 5° to 120° 2θ with steps of 0.0167° 2θ; the counting time was of 1.905 s per step.

The samples were loaded on aluminum sample holders by using a side-loading technique.

A reference silicon tablet was measured at the beginning of each measurement session, in order to test the analytical settings and to monitor the instrumental drift.

Moreover, a soil sample was randomly selected as control sample, and its XRDP spectrum was collected for each measurement session in order to evaluate instrumental variability.

2.3. Data analysis

2.3.1. Signal processing

The collected diffractograms consist of 6882 data points covering the region from 5° to 120° on the 2θ scale. Since the last part (from 91.9° 2θ) of the signal did not present any relevant peaks, it was cut considering for data analysis only 5200 experimental points (Fig. 1a). Data were successively arranged in a matrix of dimensions 240 $\times$ 5200. Signal preprocessing consisted of two steps: denoising and alignment.

Noise reduction and background correction of the XRPD spectra were achieved in wavelet domain [18,19], taking advantage of the multiresolution feature of the wavelet transform. In fact, background can be identified as a very low frequency contribution and instrumental noise as a high frequency one. To this aim an in house routine has been developed in Matlab; it operates as follows: (a) each signal is decomposed by using the discrete wavelet transform (DWT) at decomposition level ten with a daubechies 5 wavelet filter (these settings were chosen by preliminary inspection of the decomposition of a XRPD signal, testing different decomposition levels and wavelet filters of

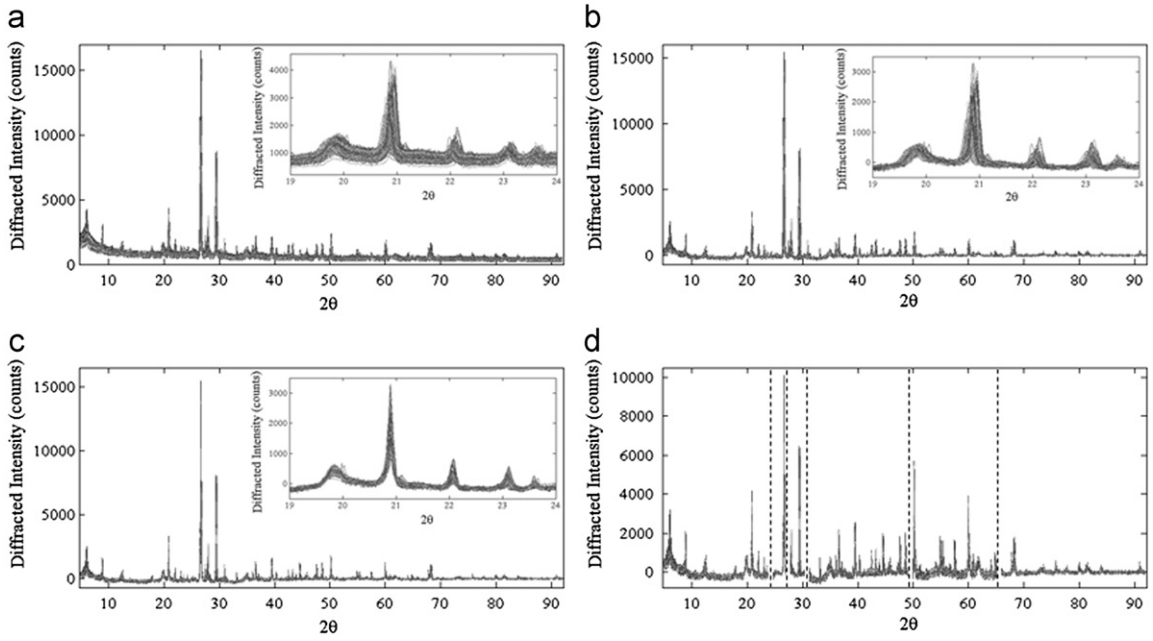

Fig. 1. Collected diffractograms of soil samples after the different data pretreatments: (a) icoshift aligned spectra (expansion from 5° to 19° 2θ); (b) after wavelet denoising procedure (expansion from 5° to 19° 2θ) and (c) after the block-scale procedure. Dotted lines mark the limits of the different scaled regions.

daubechies, symlet and coiflet families, in order to capture the best background profile in the approximations of the last considered decomposition level); (b) approximation coefficients of the 10th level were set to zero to remove the background contribution; (c) hard thresholding of details coefficients from level 1 to 10 has been applied by using a global threshold value obtained by a wavelet coefficients selection rule using a penalization method provided by Birgé–Massart [20] on the basis of the standard deviation of details coefficients of the first decomposition level [21]; (d) the preprocessed XRPD signals are obtained by reconstruction (applying inverse transform: IDWT) in the original domain of the wavelet coefficients retained after steps (b) and (c).

Fig. 1b shows the result of application of the above routine, it also includes an expansion of the area between 19° and 24° 2θ that highlights the effect of denoising and background correction.

Alignment of the signals is needed, since the horizontal shift of the peaks introduces variability among samples not imputable to real differences, as checked by replicate measurements of the same soil sample used as control during all working sessions, but to measurement handling. The handmade loading of the samples into the measuring cell and the instrumental drift that can occur during the measuring time are among the possible causes that might produce a misalignment of the same peaks in the measured XRPD. The diffractograms of the control sample (not shown) give evidence of this shift of the peaks. The spectra alignment was performed by using the icoshift algorithm [22]. The icoshift tunable parameters were set as follows: at first a preliminary alignment of the whole spectrum was sought by coshift procedure; then an interval alignment (intervals were manually chosen in order to obtain the best alignment) was carried out using as alignment target one of the data set signal. This was chosen among the spectra that the program suggested as the more similar to the medium signal. The result of this pretreatment (with the expansion from 19° to 24° 2θ) is shown in Fig. 1c.

2.4. Data scaling

The aligned, de-noised and background corrected spectra were then subjected to scaling in order to avoid only major components to contribute to the decomposition models. To this aim blockscaling [23], to "block-adjusted non-scaled data", was applied. This procedure allows peaks of minor intensity to contribute to the model without altering the relative scale of variables belonging to the same block. Fig. 1d shows the block-scaled spectra, dotted lines marks the limits of the intervals selected to define each block.

2.5. Data sets and decomposition methods

Finally, pretreated diffractograms were analyzed both by considering the three-way nature of data set (samples, spectra, depths) using PARAFAC [24] and by unfolding using PCA. In PCA analysis, a matrix consisting of 240 samples $\times$ 5200 XRPD signal points was considered; while in PARAFAC analysis a three-way array ($48 \times 5200 \times 5$) was analyzed with on Mode 1 the sampling points for each season, 48, on Mode 2 the X-ray diffraction signal points, 5200, and on Mode 3 the sampling depths, 5.

2.6. Software

The alignment of the spectra was performed by using the icoshift 1.0, freely available on 〈www.models.kvl.dk〉. Noise reduction and background correction were performed using an in house written routine based on function implemented in the Wavelet Toolbox™ 4 distributed by MathWorks (MA, USA).

PCA and PARAFAC were carried out using PLS Toolbox 6.0 distributed by Eigenvector Research Inc. (WA, USA).

3. Result and discussion

In order to investigate the presence of similarities or differences among the different geographical area, the sampling period and the sampling depth, data analysis was applied both considering each single sampling period as a data set, as well as on the overall data. Owing to the fact that results coming from the partial data sets are coherent with the one obtained from the complete elaboration, in the following, only the latter results are presented and discussed.

3.1. PCA analysis

The 240 × 5200 data matrix was pre-treated as previously explained in Data analysis section. A 2 PCs model, explained variance 75.74%, was chosen. The scores plot of the first two components is shown in Fig. 2. The first PC explains most of the variance of the model. In particular, samples of producer C differentiate along this component. Samples coming from holes 1 and 3, all sample depths (from **a** to **e**), for the three periods are located at negative values of PC1 scores, while samples coming from hole 5 (all depths and periods) are at positive values. Sampling point 4 get positive scores values for the first two periods and mostly negative for the third period. On the contrary, soil samples coming from sampling points 2 are spread from positive to negative scores values. Samples from producers A, B and D, all depths and periods, form three, not perfectly separated, clusters that are quite compact and located near the origin of the PC1 axis.

As regards the second principal component, PC2, it differentiates the hill producer (C) samples, located at positive values of PC2, from the in plain producers, located at negative values (producer B) or close to zero (producers A and D). According to PC2 scores values it is possible to discriminate samples with a different geographical localization.

A further insight about the samples positioning/grouping can be made by considering the loadings plots, Fig. 3. To gain a better interpretation these are represented as line plots per each component, on the 2θ scale, and are on a color scale according to the values of correlation/congruence loadings [25]. The congruence loadings express the correlation among the original variables and the latent variables resulting from the model. In particular, they represent the modeled variance by each variable. The closer a color of a variable is to red (positive) or blue (negative) the more important the variable is to explain the differences observed among the samples.

Furthermore, a preliminary identification of the diffractogram peaks was considered as well, in order to recognize the mineral phases that mainly influence the discrimination among different soils.

The intra site distinction of the hill samples, observable on PC1 for producer C, is mainly due to a different quantity of quartz and calcite in the samples; in fact, the XRPD regions where these components are located give the main contribution to PC1 loadings as shown in Fig. 3a. A certain degree of soil's variability at the site of producer C (hill area) was also noticed during the on field sampling. This area is known to be characterized by a great complexity and heterogeneity of the soils, as regard to both origin and composition. Soil sparsely calcareous originated hundreds of thousands of years ago from silty clay sediments of rivers lies close to calcareous soil formed from clay rocks with sandy intercalation of Pliocene age (5–25 million years ago) [26].

On the contrary, in-plain samples result to be less scattered and so more homogeneous, both relative to sampling points and depths.

On the other hand, the differences between hill and in-plain regions are highlighted along PC2, whose loadings, shown in Fig. 3b, are characterized by contribution of clay, which seems to be mainly responsible for this discrimination. As far as the presence of other peaks is concerned, quartz and calcite show high value of loadings, but the color indicates low correlation, i.e. a small amount of variance of these variables explained by PC2; thus the variation of these phases can be considered of scarce importance for the differentiation of the samples observed along PC2 in the scores plot.

These results confirm the geo-morphological criteria of classification of the province of Modena. In fact, on these bases, the plain zone is distinguished by the presence, and the age, of fluvial terraces and the basin domain of the main rivers (Po, Secchia and Panaro and their minor tributaries along the Apennine margin) that are relevant for mineral association of the alluvial sediments.

As the seasonal variability is concerned, from this elaboration it appears to be of little importance, because the samples relative to the three different sampling periods present similar trend and are almost placed in the same positions of the scores plot (Fig. 2). Moreover, the observed differences among the same sample in the three seasons have almost the same dispersion of the repeated measures of the control sample (not reported in the plot). The only valuable exception regards the samples of point 4 concerning producer C that, for the last sampling period, result to be located in a different position, that is at lower values of PC1. This difference cannot be attributed with certainty to a seasonal variability, since no evidence for other samples have been observed; hence, this behavior could be due to the great complexity and heterogeneity of the soil in this particular field, also associated with not exactly reproducible sampling GPS position.

Moreover, to assess the influence of the alignment procedure of the data, a PCA analysis was also conducted on the 240 × 5200

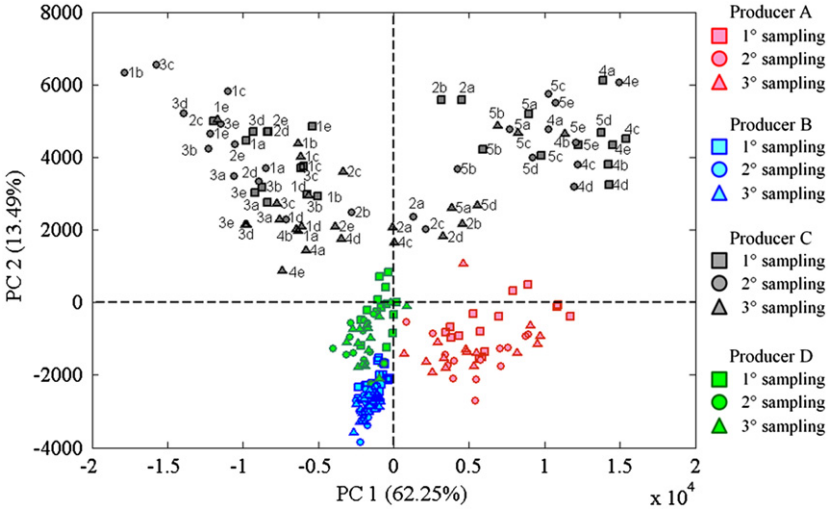

Fig. 2. Scores plot, PC1 vs. PC2, for all the collected diffractograms. Colors indicate different producers (or sampling area), red A, blue B, gray C and green D; symbols indicate the sampling periods, first sampling spring 2009 □, second sampling summer 2009 ○ and third sampling winter 2009/2010 Δ. Labels identify the sampling points in the field and the sampling depth, from **a** to **e**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

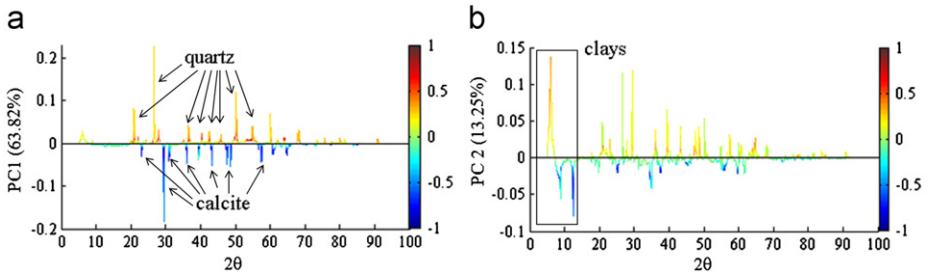

Fig. 3. PC1 (a) and PC2 (b) loadings plots vs. 2θ values. The loadings profiles are colored according to the values of congruence loadings. The coding of the color is shown in the color bar. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

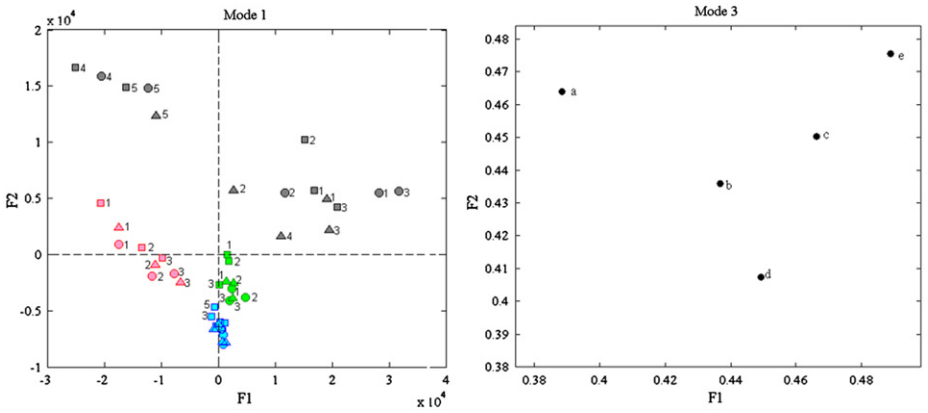

Fig. 4. PARAFAC scores plot (Mode 1, sampling points) F1 vs. F2 and loadings plot (Mode 3, sampling depths) F1 vs. F2, with centering across Mode 1. In Mode 1 colors indicate different producers (or sampling area), red A, blue B, gray C and green D; symbols indicate the sampling periods, first sampling spring 2009 □, second sampling summer 2009 ○ and third sampling winter 2009/2010 Δ. Labels refer to the sampling points in the field for the four producers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

data matrix of the non-aligned diffractograms. The results, data not reported, show that PC1 mainly distinguishes the three time periods in which the samples were collected and measured. Because of this source of variability the PC2 vs. PC4 scores plot must be considered to recover the observed grouping, albeit less clear, with respect to the provenience of samples, observed in PC1 vs. PC2 scores plot of aligned data (Fig. 2). Therefore, it is possible to confirm that the used alignment procedure did not introduce artifacts in samples differentiation.

3.2. PARAFAC model

In order to evaluate if there is a common variability profile with respect to depth in the different sampling sites, the PARAFAC method was used on the three-way array sampling points for the different sampling periods in Mode 1, XRPD spectra on Mode 2 and sampling depth on Mode 3.

Two different centering procedures were compared: (a) centering across Mode 1, i.e. unfolding the data array to $I \times JK$ and removing means from JK columns, in this way variability with respect to sampling site (producer) is enhanced, and (b) across Mode 3, i.e. unfolding the data array to $K \times IJ$ and removing means from IJ columns, so that variability with respect to depth is enhanced. In the first case, the scores plot for the first Mode 1 (Fig. 4) results similar to that of PCA analysis and the loadings plot of Mode 3 shows no trend or clusters relatively to the sampling depths (2 Factor model; explained variance: 69.78%; core consistency: 99%). By centering across Mode 3, a 2 factors model with explained variance of 23.03% and core consistency of 100% was obtained. In this case, Mode 3 loadings plot (Fig. 5) shows the depths clustered with respect to upper (a and b) and lower (c, d and e) fractions on Factor 1, but from the Mode 1 plot (Fig. 5) it results that this is mainly due to hill samples, and in particular to sampling point 5 and point 2, which shows a great variability on the three sampling periods as captured also by Factor 2. From Mode 2 loadings plot (Fig. 6), it is possible to see at positive values of Factor 1 the peaks relative to calcite, whilst at negative values those of quartz. The analysis reveals that the upper fraction of point 5 differs from the lower one because of the greater content of calcite and a smaller quantity of quartz. The opposite situation occurs for point 2. The seasonal variability of point 2, explained along the second factor, is mainly due to a different presence of quartz and calcite, confirming what was previously stated about in-plain soils of Modena district.

The other points lay very close to the origin of the axes, meaning that they are scarcely influenced by the sampling depth, owing to the "homogeneity" of the soils along the depth profile.

On the basis of these results sampling depth variability seems to be neglectful for in-plain soils, hence averaging samples with respect to depth seems reasonable, but could be worth to consider distinct sampling of at least an upper (10–30 cm) and a lower (30–60 cm) section, as far as hill samples are concerned.

These final considerations are also supported and confirmed by the chemometric analysis carried out on the metals content evaluated on the same soil samples limited to the first sampling period in a parallel study by our research group (data not reported). In fact, results from PCA performed on the metals content namely, Na, K, Ca, Mg, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Th and U determined on the HNO_3 extractable fraction from soil for the same soils samples, showed an almost identical discrimination of the producer sites and sampling depth. Moreover, the same pattern in soil samples differentiation has also been observed with respect to the values of $^{87}Sr/^{86}Sr$ isotopic ratio [11].

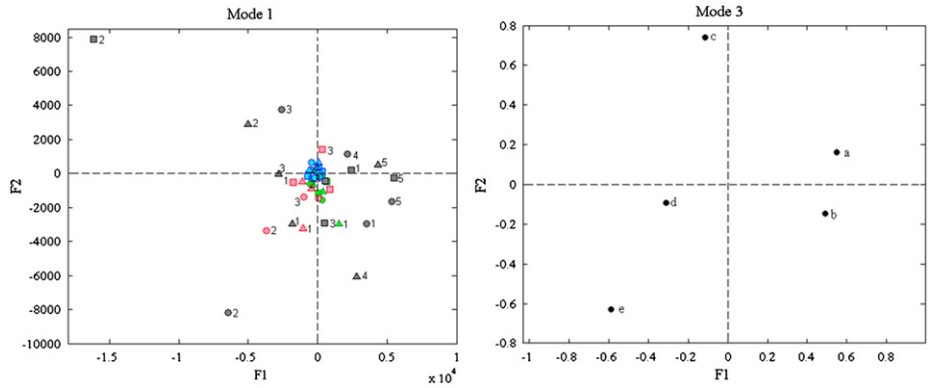

Fig. 5. PARAFAC scores plot (Mode 1, sampling points) F1 vs. F2 and loadings plot (Mode 3, sampling depths) F1 vs. F2, with centering across Mode 3. In Mode 1 colors indicate different producers (or sampling area), red A, blue B, gray C and green D; symbols indicate the sampling periods, first sampling spring 2009 □, second sampling summer 2009 ○ and third sampling winter 2009/2010 Δ. Labels refer to the sampling points in the field for the four producers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

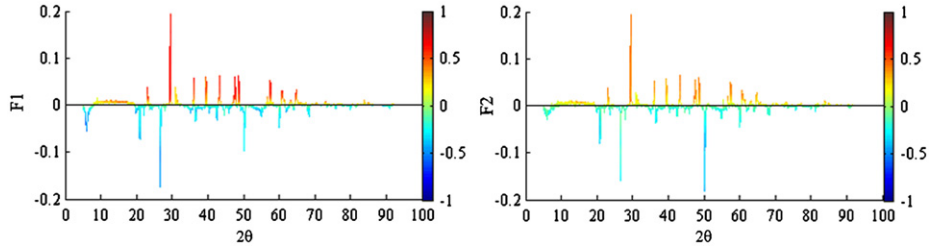

Fig. 6. PARAFAC (model obtained with centering across Mode 3) loadings plots (Mode 2, XRD signals) vs. 2θ values: (a) F1 and (b) F2. The loadings profiles are colored according to the values of congruence loadings. The coding of the color is shown in the color bar. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

In this study the key role of the soil sampling procedure for geographical traceability investigation is considered. Soil variability, intra-site, extra-site and along the sampling depth profile, was examined by means of soil XRPD profiles and chemometric techniques. All the analyzed soil samples were collected both on in-plane and hill areas of the province of Modena.

Results show that hill samples are characterized by a fairly broad intra- and extra-site variability and, in a less extent, also along the sampling depth profile. On the contrary, samples coming from the in-plane areas of Modena province resulted to be more homogeneous even from the vertical profile. Moreover, the results obtained so far do not reveal a "significant influence" of the sampling period.

The practical implications of this pilot survey are of fundamental importance in order to plan the number of soil samples and their type (i.e. single soil carrot or fractionated ones, split in upper and lower parts) for the extensive sampling on the entire province of Modena for the geographical traceability of typical food.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.06.067.

References

[1] S. Kelly, K. Heaton, J. Hoogewerff, Trends Food Sci. Techol. 16 (2005) 555–567.
[2] C.M.R. Almeida, M.T.S.D. Vasconcelos, J. Agric. Food Chem. 51 (2003) 4788–4798.
[3] M. Brunner, R. Katona, Z. Stefánka, T. Prohaska, Eur. Food Res. Technol. 231 (2010) 623–634.
[4] D.G. Asfaha, C.R. Quetel, et al., J. Cereal Sci. 53 (2011) 170–177.
[5] 〈www.trace.eu.org/je/belgium/lectures.php〉.
[6] 〈www.progettoager.it〉.
[7] R. Margesin, F. Schinner, Manual of Soil Analysis: Monitoring and Assessing Soil Bioremediation, first ed., Springer, Germany, 2005.
[8] M.R. Carter, E.G. Gregorich, Soil Sampling and Methods of Analysis, second ed., Taylor & Francis Group, Boca Raton, 2006.
[9] T. Prohaska, W.W. Wenzel, G. Stingeder, Int. J. Mass Spectrom. 242 (2005) 243–250.
[10] S. Holzl, Sr isotopes as a tool for provenancing,in: Proceedings of the Final TRACE Conference, Lectures: How to TRACE the origin of food?, 2009 〈www.trace.eu.org/je/belgium/lectures.php〉.
[11] C. Durante, C. Baschieri, L. Bertacchini, M. Cocchi, A. Marchetti, S. Sighinolfi, M. Silvestri, Anal. Chem., in preparation.
[12] A. Taylor, S. Branch, M.P. Day, M. Patriarca, M. White, J. Anal. At. Spectrom. 26 (2011) 653–692.
[13] L.J. Moens, F. Vanhaecke, D.R. Bandura, V.I. Baranov, S.D. Tanner, J. Anal. At. Spectrom. 16 (2001) 991–994.
[14] M. Barbaste, K. Robinson, S. Guilfoyle, B. Medina, R. Lobinski, J. Anal. At. Spectrom. 17 (2002) 135–137.
[15] Decree of 27 July 2009 published on O.J. no. 187 of 13 August 2009.
[16] CE Regulation no. 813 of 17 April 2000.
[17] D.R. Smart, E. Schwass, A. Lakso, L. Morano, Am. J. Enol. Vitic. 57 (1) (2006) 89–104.
[18] B. Walczak (Ed.), Wavelet in Chemistry, Elsevier, Amsterdam, NL, 2000.

[19] R.R. Coifman, Y. Meyer, M.V. Wickerhauser, in: Y. Meyer, S. Roques (Eds.), Progress in WaVelet Analysis and Applications, Editions Frontieres, France, 1993.
[20] L. Birgè, P. Massart, in: D. Polard (Ed.), Festschrift for L. Le Cam, Springer, Germany, 1997, pp. 55–87.
[21] M. Misiti, Y. Misiti, G. Oppenheim, J.M. Poggi, Wavelet Toolbox™ 4 User's Guide, The MathWorks, Inc., Natick, MA, 2010.
[22] F. Savorani, G. Tomasi, S.B. Engelsen, J. Magn. Reson. 202 (2010) 190–202.
[23] S. Wold, E. Johansson, M. Cocchi, in: Hugo Kubinyi (Ed.), 3D QSAR in Drug Design: Theory, Methods and Applications, ESCOM Science Publishers, Leiden, 1993.
[24] R. Bro, Chemometr. Intell. Lab. 38 (1997) 149–171.
[25] G. Lorho, F. Westad, R. Bro, Chemometr. Intell. Lab. 84 (2006) 119–125.
[26] G. Nigro, M. Zamboni, et al., La zonazione viticola della provincia di Modena, CRPV, Provincia di Modena, 2008.