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Visible Near Infrared Spectroscopy as a Green Technology: An Environmental Impact Comparative Study on Olive Oil Analyses

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Abstract: The olive oil industry is a significant productive sector in the European Union and the related production process is characterised by practices and techniques associated with several adverse effects on the environment. In the literature, many works on the environmental impact assessment of the olive oil chain have been carried out but the effects of the analytical analyses procedures were considered to be negligible. Currently, the reduction of solvents and of energy consumption in the laboratory has become a crucial aspect to be investigated. In this scenario, non-destructive optical methods based on visible/near-infrared (vis/NIR) spectroscopy represent a simple, rapid, and easy-to-use method to predict olive and olive oil quality parameters. Therefore, the aim of the work was to evaluate the environmental impact of the use of optical vis/NIR technologies for analytical assessment in comparison to chemical analyses on olive oil. The life cycle assessment method (LCA) was used. The functional unit defined for this study was the analysis and a “from cradle to grave” approach was applied. The vis/NIR technology results were distinctly better, by 36 times on average, than the chemical methods. Attention must be paid to the calibration phase of the vis/NIR instrumentation: In this case, the two methods must coexist for this initial procedure to obtain the required reference data for a reliable chemometric model. In conclusion, the vis/NIR spectroscopy gives very reliable results and can be considered a green technology, representing a choice among applications of low environmental impact analytical technologies.

Keywords: olive oil; analysis methods; vis/NIR; chemical; sustainability; life cycle assessment

1. Introduction

EU olive oil production in the last harvest campaign (2018/2019) reached 2101 thousand tonnes of final product (69.7% of worldwide production). Considering the harvesting campaigns from 2012/2013 to 2016/2017, the EU produced 67%, consumed 55%, and exported 67% of the world’s olive oil. Shifting to the economic value of this sector, in the last years, the EU olive oil production reached a value of five billion euros, 80% of which was obtained only from Spain and Italy [1,2]. Olive oil not only represents a significant sector in the EU economy but is also of importance all over the world.

The production of olive oil is associated with several negative effects on the environment, e.g., depletion of resources, soil degradation, atmospheric emissions, and waste production [3,4]. Regarding the sustainability of olive oil production, environmental impact analyses have been carried out throughout the production chain, from the agricultural phase, through the transformation, to product

consumption, and waste treatment [5]. The agricultural sector, with its activities of farming, use of fertilizers, herbicides, and pesticides, was defined as the one with the greatest accountability for the environmental impact [6–10]. This phase is the largest contributor to the whole olive oil production chain. The major impacts of the cultivation phase are due to soil management, pruning, harvesting, production, and the use of fertilizers and plant protection products, and also due to irrigation [11,12]. Considering olive oil production as a whole, the practices of effluent disposal, due to groundwater contamination, could be defined as the major hotspot in the whole production chain [6]. The milling by-products can affect the environment. These by-products, when re-used as fuels or fertilisers, could provide a significant positive contribution in terms of environmental credits by avoiding the need for the production of chemicals [8,13]. The environmental impacts of the olive oil industry may vary significantly depending on different techniques and practices in oil production processes and on regional conditions [14]. The “sustainable production” can be identified in the initial stages of the agricultural operations if integrated and organic production methods are used [15]. The transformation phase can be also defined as sustainable if all the activities take care of reducing energy and water consumption and paying attention to the incidence of packing and shipping [16]. Despite the high interest in environmental impacts in the olive oil production chain, few studies are available concerning the impact of the laboratory analyses performed on different products such as olives, olive paste, olive oil, and by-products (e.g., pomace and wastewater).

These analyses are carried out in laboratories constantly and are fundamental to obtain (i) a value that can be related to the quantity of olive oil, and (ii) related quality indices to identify olive oil quality [17]. The spots where these analytical activities can be performed can be identified along the production chain (from the farm to the final use), as shown by grey arrows in Figure 1. The analyses can be performed on the olives during the farming period to monitor the olives’ ripeness, and at the mill receiving them, to estimate the maximum extraction quantity of oil. Moreover, the analyses performed on olive oil samples can be carried out at different points along the whole production chain such as (i) immediately after the extraction phase, (ii) during storage, and (iii) before selling, to evaluate and control quality parameters. These analyses represent an efficient method to evaluate farming, harvesting, milling, and storing activities. Analyses on the finished product define olive-oil quality parameters and allow us to classify the products using the commercial definitions (olive oil, virgin olive oil, and extra-virgin olive oil). Moreover, the same analyses can be used to identify commercial frauds such as olive oil adulteration using other vegetable oils, which compromise the authenticity of the olive oil. The official methods defined by the Association of Official Agricultural Chemists (AOAC) [18] fixed the procedures for olive oil analyses. Even if a step-by-step procedure controls the methods, different factors such as time, energy power absorption, and chemicals usage may represent criticisms in the practical application. The different methods require different timings to obtain the results (from minutes to days) depending on the analysis. Moreover, the more time that is needed to obtain the results, the more the instrument absorbs electric power, and the chemicals required potentially represent a risk due to their usage and disposal, for both operators and the environment.

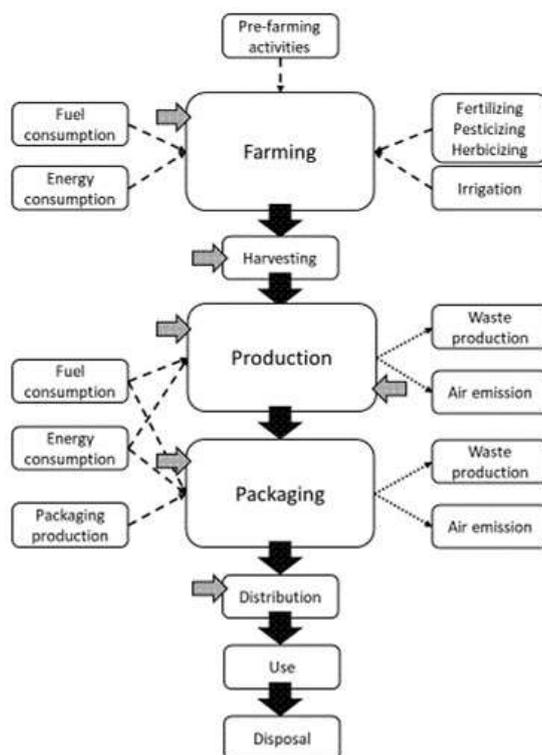


Figure 1. The olive oil production chain and the spots (grey arrows) where analyses can be performed.

Nowadays the reduction of solvents used and of energy consumption has become a crucial aspect to be investigated. In this scenario, non-destructive optical methods based on visible/near-infrared (vis/NIR) spectroscopy represent a simple, rapid, and easy-to-use method to predict quality parameters and hence for objectively evaluating indices of different fruit and vegetable products [19,20]. During vis/NIR spectroscopy measurement, light radiation illuminates the sample that absorbs a specific quantity of radiation and reflects another part at specific wavelengths, depending on the sample matrix features. The vis/NIR detector records the specific quantity of vis/NIR light reflected or transmitted after the interaction between light and sample and translates it into a spectrum [21]. Peaks and valleys of the spectra can be correlated to chemical parameters using chemometric techniques for the calibration of predictive models. Once calibrated, a vis/NIR device can analyse samples in a non-destructive way and in few seconds, without sample processing and without expert personnel trained to use complex laboratory instrumentation. Compared to vis/NIR technology, chemical techniques are time-consuming, require sample preparation and the use of chemical reagents, and they are also expensive due to the need for expert laboratory technicians (Table 1) [22].

Table 1. Comparison between vis/NIR and chemical analysis highlighting the peculiar aspects.

	Vis/NIR Analysis	Chemical Analysis
Rapidity	X	-
More parameters analysed at the same time	X	-
Non-destructive analysis	X	-
Direct measurement	-	X
Accuracy	High number of samples required	X
Use of chemicals	-	X

In the literature, vis/NIR spectroscopy was applied on intact olives just before milling or during the milling process to predict crucial parameters such as physical indices (i.e., yield point force and

total deformation energy), chemicals (moisture, oil, and sugars content) and maturity index (MI), for an optimization of the process [23–25]. The application of vis/NIR spectroscopy is not only used on solid samples, but it can also be applied to liquids. Sinelli et al. [26] applied NIR spectroscopy as a rapid tool to classify extra virgin olive oil based on fruity attribute intensity while Wesley et al. [27] and Christy et al. [28] used NIR spectroscopy for the detection and quantification of adulteration in olive oil. Moreover, in recent years, research tends to pay attention to on/in/at-line applications and vis/NIR spectroscopy offers several opportunities for quality control during the process, by performing measurements on olive fruits, on pastes, and on oils [29,30]. The replacement of the analytical tools and reagents related to chemical analyses with one vis/NIR spectrometer could be envisaged based on published works [31] and could reduce the environmental impact of analyses.

In order to define vis/NIR spectroscopy as a green technology, it is necessary to focus the attention on sustainability aspects. The environmental impact of vis/NIR spectroscopy can be assessed using a life cycle assessment (LCA) [32]. LCA was initially applied to the manufacturing sector, and currently it is increasingly being applied to food production systems [33]. LCA was also used to compare the environmental performance inside the olive oil chain [6,15]. Avraamides and Fatta [6] considered in their study fertilizers and pesticides production, the agricultural processes, the industrial processing, transportation, and waste management identifying as the main hotspots of the chain the effluent disposal from olive mills and the fertilizers production. Notarnicola et al. [15] compared the conventional and the organic production of extra virgin olive oil; the organic system results five times more eco-compatible due to the use of pesticides in the conventional one.

The aim of the work is to calculate the environmental impact of the crucial analyses for the control of the qualitative parameters of olive oil. Chemical analyses were analysed and vis/NIR spectroscopy was considered as an alternative methodology to replace chemical analyses in the oil sector [34,35]. Finally, a comparison was performed between the environmental impact of the chemical analyses and the vis/NIR spectroscopy analysis.

2. Materials and Methods

The life cycle assessment (LCA) method was developed in compliance with the international standards of series ISO 14040 [36]. It represents a holistic method of assessing the environmental impacts and resources used throughout the life of a product, from raw materials extraction to waste treatment, through the transformation and the use of goods [36].

2.1. Goal and Scope Definition

The goal of the study was to compare the environmental impact of the chemical analyses and the vis/NIR spectroscopy analysis of crucial parameters of olive oil. Three parameters were chosen as being among the most representative and capable of characterizing oil quality: (i) Acidic composition, analyzed using the gas-chromatographic method of methyl esters; (ii) peroxides, analyzed using the iodometric method; (iii) tocopherols, analyzed using the high-pressure liquid chromatography (HPLC) method with the fluorescence detector [18]. The identification of the impact assessment was performed for both the chemicals (destructive analyses) and the vis/NIR spectroscopy (optical, non-destructive analyses). For each analysis, indirect environmental impact related to energy source generation, tools, and raw materials supply were calculated.

2.2. Functional Unit

According to ISO standards, the functional unit is defined as the main function of the system expressed in quantitative terms [36]. In a comparative study the main aspect is the identification of a functional unit that allows us to compare different systems. In this study, the functional unit was defined as the pool of analyses necessary to obtain the three parameters.

2.3. Definition of the System

The different nature and procedures related to the chemical and optical analyses allowed us to define the reference flow for the two methods. In the chemical one, the analysis was intended as the set of activities necessary to obtain three results related to three chemical parameters. Regarding the vis/NIR spectroscopy, the analysis defined the procedure to obtain three indices related to the three chemical parameters.

Inputs and outputs of the system were defined by carrying out some interviews at five laboratories located in different areas of Italy (Teramo, Milano, Reggio Calabria, Sassari, and Bari) and the following conclusions for applying to the comparisons were reached:

- The productivity of the laboratory was set to 2000 analyses year⁻¹, identified as the capacity of a medium size laboratory.
- For every electronic tool a lifetime was defined as equal to 10 years.
- Three hundred working days per year were considered as the working time of the laboratory, deriving a daily productivity equal to 6.66 samples day⁻¹.

The laboratories under study were equipped with analytical tools necessary for olive and olive oil analyses. The working capacity of all the machines inputted was 2000 analyses year⁻¹. For those analytical tools that were also used for analyses different from the olive oil one, an allocation was applied (Section 2.5).

Regarding the transport of the tools, a hypothetical average amount of kilometers “from the factories to the laboratories” was allocated to the number of analyses (20,000 analyses) performed in the life-time of the tools (10 years). From a screening study, it represents less than 1% in all the impact categories due to the allocation procedure, and therefore it was ignored. For the transport of the samples “from the mill to the laboratory”, no substantial differences could be attributed depending on the type of analysis performed, so according to the comparative aim of the study this transport was also ignored.

All the inputs and outputs were assembled in seven groups for simplification purposes:

- “Analytical tools”: The devices requiring an electrical supply to operate (i.e., HPLC, gas-chromatograph, computers, hood, vis/NIR system, etc.).
- “Energy”: The electric energy necessary for the analytical tools.
- “Laboratory materials”: The tools which do not need an electric supply (vials, glass components, syringes, spare parts, etc.).
- “Chemicals”: Chemical substances and reagents (hydrogen, nitrogen, heptane, acetic acid, chloroform, etc.).
- “Calibration”: The pool of chemical analyses performed to obtain the predictive model fundamental for the vis/NIR analyses.
- “Water”: The amount of tap water.
- “Waste treatment”: End of life scenario for all the inputs used in all the analyses.

2.4. System Boundaries

A “cradle to grave” approach was chosen. Figure 2 shows the reference flow of the two analysis methods. The “cradle to grave” approach allowed us to consider different factors from the extraction of the raw materials, the construction of the tools, the production of laboratory materials, the chemicals, and the calibration for the vis/NIR analyses (up-stream). It included the core of the study, defined as the pool of three chemical analyses for the chemical approach and one optical analysis used to evaluate three chemical parameters for the optical approach. Moreover, in the downstream, this approach considered the disposal of every single component entered in the system with different waste management scenarios.

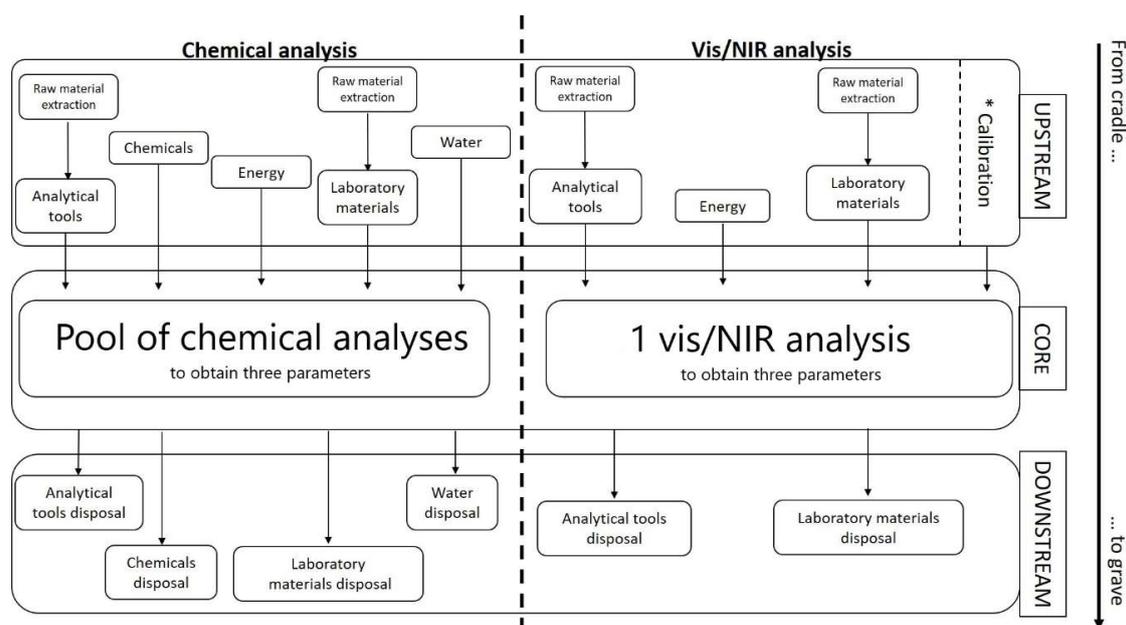


Figure 2. System boundaries and elements flow. *Calibration = chemical analyses + vis/near infrared (NIR) analyses.

2.5. Life Cycle Inventory (LCI)

The inventory phase is based on the step-by-step procedures regarding the chemical analyses: AOAC and European Regulation standards help to identify the input and output of the system. Due to these standardised methods, the times, sequences of activities, and chemicals used were defined.

The analytical tools were deconstructed and analyzed for their raw materials. The energy consumption and the time of usage for all the analytical tools were identified and reported in Table 2. The electric and electronic parts of the analytical tools were considered electronic components (46% of steel, 32% of plastics, 14% of printed wiring boards, and 8% of cables).

Table 2. Weight, power, and usage time of the analytical tools necessary for the execution of the olive oil analyses.

Analytical Tool	Materials	Weight (kg)	Power (kW)	Time (hour)
HPLC	Electronic components	60	0.160–0.320	1.5
	Stainless steel	10		
Computer	Electronic components	13	0.13	0.33–1.5 *
Vis/NIR spectrometer	Electronic components	14	0.24	0.33
	Glass fiber	1		
Balance	Electronic components	3	0.13	0.16
	Stainless steel	2		
Gas-chromatograph	Electronic components	40	0.5–2.0	1.33
	Stainless steel	10		
Suction hood	Glass	20	0.44	0.25–0.75 *
	Stainless steel	20		
	Electronic components	15		

* Different times depending on the type of analysis.

When a chemical analysis is performed some reagents must be used. These substances were declared in the standards. Table 3 shows the chemicals and the relative amounts used for the selected chemical analyses.

Table 3. Chemicals for the different analyses.

Analysis	Chemicals/Reagents	Amount (mL)
Acidic composition	Potassium hydroxide solution	0.2
	Hydrogen	300
	Nitrogen	300
	Heptane	2
Peroxide	Acetic acid	45
	Potassium iodide	3
	Nitrogen	700
	Sodium thiosulfate	18
	Chloroform	30
Tocopherols	Butyl acetate	3
	Hexane	94

The amounts reported in Table 3 represent the quantity of chemicals necessary to perform one analysis, which includes the execution of three replicates for each analysis. The output derived from the execution of the analysis is considered as hazardous waste and needs a specific waste management practice.

Conversely, no chemicals were used for performing the vis/NIR analysis. Moreover, the composition of the optical instrument is simple (approximately 94% electronic components, 6% glass fiber). For this study were considered spectra acquisition performed at room temperature (20 ± 0.5 °C), in transmission mode in the spectral range 12,500–4000 cm^{-1} employing vials with an 8 mm path length and a NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany) [37]. A crucial aspect regarding the NIR spectroscopy consists in the calibration phase, a fundamental procedure that must be performed before the application of the optical analysis and also at intervals throughout all the life cycle of the optical vis/NIR system to reinforce the predictive model. A conventional calibration procedure was considered with pre-treatment of spectra (smoothing + standard normal variate) and calculation of the model using the partial least square (PLS) algorithm. For validation a test set validation was considered with a dataset split into 62% training set and 38% validation set [37]. Referring to the life-time assumed (10 years), a total of 700 analyses were defined for every parameter, divided into 500 analyses to create the predictive model (calibration and validation), and 200 (spread over the 10 years) to reinforce the same. Each NIR analysis refers to a pool of three parameters, therefore a total of 2100 chemical analyses were assumed as reference analyses to build and maintain the predictive PLS model.

2.6. Allocation Procedures

In the laboratories analyzed, some of the analytical tools were used for more than one type of analysis (i.e., balance, computer, and the suction hood). An allocation procedure was applied. Table 4 shows the allocated value for every input related to the chemical and vis/NIR analyses. The quantity (Q) identifies the amount of input that could be expressed in mass, volume, or energy values. In order to obtain the allocated value (Av), a two-step allocation procedure was performed. The allocation factor (Af) goes from 0 to 1 and expresses an allocation value in term of usage time. The life-time (Lt) identifies the number of analyses the product can perform during its life-time.

Table 4. Quantity, allocation factor, life-time, and allocated value of the inventoried inputs and outputs.

	Input	Quantity	Allocation Factor	Life-Time (Analysis)	Allocated Value	Unit of Measure
ACIDIC COMPOSITION OLIVE OIL	Balance	5	0.12	20,000	0.00003	kg
	Suction Hood	5	0.5	20,000	0.000125	kg
	Gas-chromatograph	50	1	20,000	0.0025	kg
	Computer	13	1	20,000	0.00065	kg
	Carbon Filter	5	0.5	2000	0.00125	kg
	Capillary	220	1	2000	0.11	g
	Potassium Hydroxide	0.2	1	1	0.2	mL
	Heptane	2	1	1	2	mL
	Hydrogen	300	1	1	300	mL
	Nitrogen	300	1	1	300	mL
	Tap Water	2	1	1	2	L
	Electricity	4.44	1	1	4.44	kWh
Hazardous waste	300	1	1	300	mL	
PEROXIDE OLIVE OIL	Suction Hood	55	1	20,000	0.00275	kg
	Balance	5	0.12	20,000	0.00003	kg
	Glass Laboratory Kit	18	1	20,000	0.0009	kg
	Carbon Filters	5	1	2000	0.0025	kg
	Acetic Acid	45	1	1	45	mL
	Potassium Hydroxide	3	1	1	3	mL
	Nitrogen	700	1	1	700	mL
	Sodium Sulphate	18	1	1	18	mL
	Chloroform	30	1	1	30	mL
	Electricity	0.35	1	1	0.35	kWh
Hazardous waste	320	1	1	320	mL	
TOCOFEROLS OLIVE OIL	HPLC	70	1	20,000	0.0035	kg
	Computer	13	1	20,000	0.00065	kg
	Suction Hood	55	0.5	20,000	0.001375	kg
	HPLC Column	210	1	2000	0.105	kg
	Carbon Filter	5	0.5	2000	0.00125	kg
	Butyl Acetate	3	1	1	3	mL
	Hexane	94	1	1	94	mL
	Electricity	0.799	1	1	0.799	g
	Hazardous waste	100	1	1	100	mL
Vis/NIR OLIVE OIL	Vis/NIR	15	0.5	20,000	0.000375	kg
	Capsule	30	1	20,000	0.0015	g
	Computer	13	0.5	20,000	0.000325	kg
	Electricity	0.12	1	1	0.12	kWh

To obtain the Av of each input the following Equation (1) was used:

$$Av = \frac{Q \times Af}{Lf} \quad (1)$$

2.7. Life Cycle Impact Assessment (LCIA)

The international reference life cycle data system midpoint method (ILCD) [38] was used and the results were expressed in the following impact categories as reported in Table 5.

Table 5. Impact categories.

Impact Category	Unit of Measure	Acronyms
Climate change	kg CO ₂ eq	CC
Ozone depletion	kg CFC-11 eq	OD
Human toxicity, cancer effects	CTUh	HT-C
Human toxicity, non-cancer effects	CTUh	HT-NC
Particulate matter	kg PM _{2.5} eq	PM
Ionizing radiation	kBq U235 eq	IRHH
Photochemical ozone formation	kg NMVOC eq	POF
Terrestrial ecotoxicity	molc N eq	TE
Freshwater eutrophication	kg P eq	FE
Freshwater ecotoxicity	CTUe	FEco
Land use	kg C deficit	LU
Mineral fossil and renewable resources depletion	kg Sb eq	RD

The data processing was performed using Sima-Pro software (version 8.5) (PRé Sustainability, Amersfoort, The Netherlands).

3. Results and Discussion

The chemical analyses and the vis/NIR spectroscopy were analyzed separately and then compared. Regarding chemical analyses, Figure 3 represents the subdivision of the environmental impacts among the different factors that enter in the system analyzed (a) and among the pool of chemical analyses studied (b).

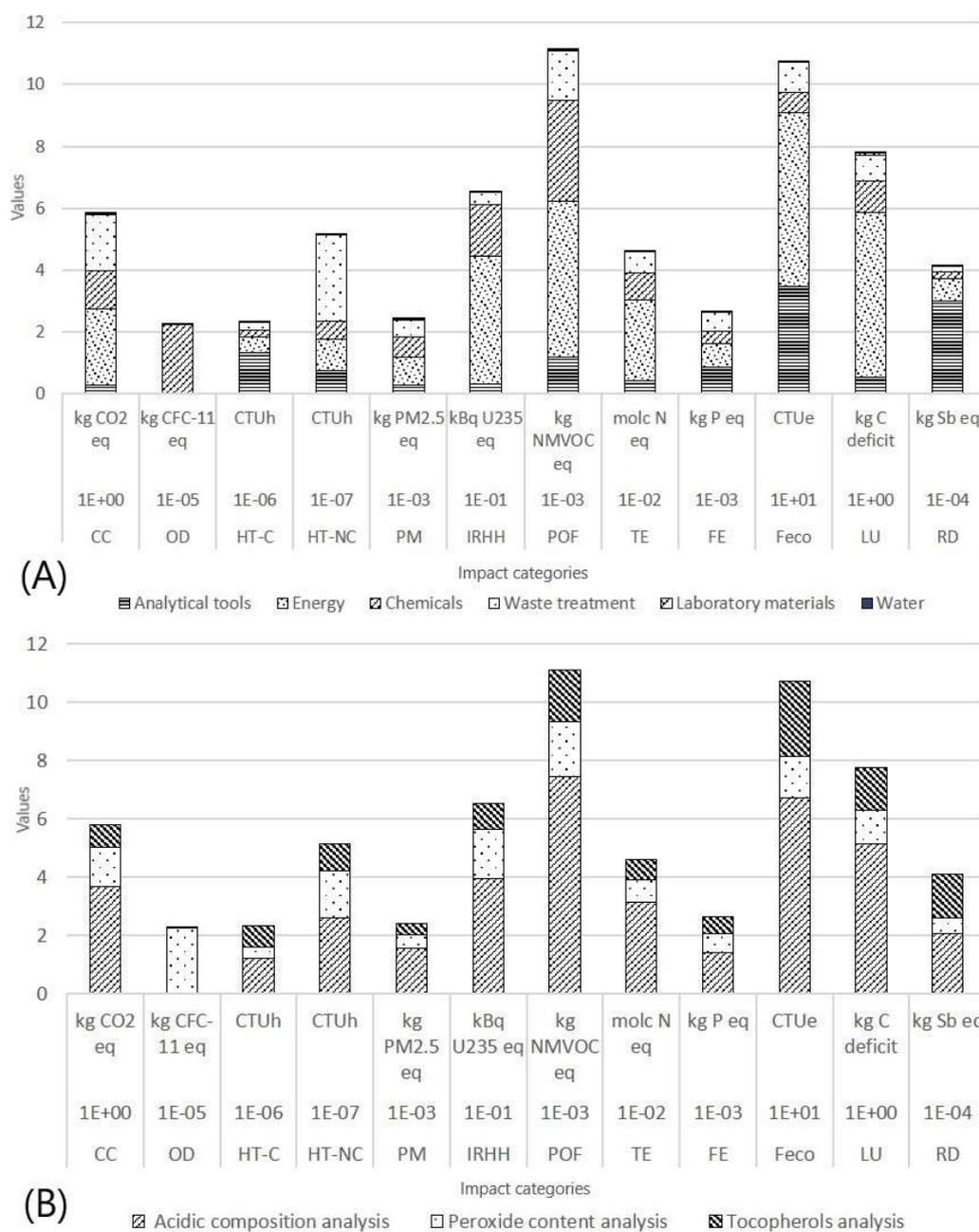


Figure 3. Impact assessment related to the execution of the pool of three chemical analyses considering a factors subdivision (A) and the type of analysis subdivision (B).

All the impact categories are related to the relative unit of measurement, allowing us to quantify the environmental impact of the execution of the pool of three chemical analyses and, at the same time, to easily identify the hotspots for both factors and analysis type.

In Figure 3a the factor “energy” reached high values for the impact categories climate change (CC) 41%, particulate matter (PM) 37%, ionizing radiation (IRHH) 63%, terrestrial ecotoxicity (TE) 56%, land use (LU) 68%, and freshwater ecotoxicity (FEco) 52%. This large contribution depended on (i) the energy demand from the analytical tools and (ii) on the Italian energy country mix, where the total energy production was attributed mostly to natural gas (45%), followed by hydropower (14%), and coal (12%). The energy derived from renewable resources covered 37% of the total electricity production.

The factor “analytical tools” contributed mainly to the impact category human toxicity, cancer effects (HT-C) with 57% and to the mineral fossil and renewable resources depletion (RD) category

with a percentage equal to 72%. The high contribution to these impact categories was linked to the production of the analytical tools. The construction of steel machinery implied a depletion of the mineral resources strictly linked to the steel extraction and a production of potentially carcinogenic products due to the steel transformation.

Another important factor contributing to the whole environmental impact was “chemicals”. These reagents were necessary to perform the chemical analyses but, at the same time, the production (chemical industries processes) implies a large amount in some of the impact categories as for the ozone depletion (OD) with a percentage equal to 98%.

The last main hotspot was “waste treatment”. The disposal of chemical substances or exhaust products after the analyses required different methods of waste treatment, and some were considered hazardous waste. The high level of this factor was recorded in the impact category HT-C with a percentage equal to 54%.

Analogous considerations could be reached focusing the grouping on the type of analysis as factors. Figure 3b reports the subdivision of the environmental impacts in term of analysis type. The hotspots, in this case, depended on the considered impact category. The analysis showing the higher responsibility was the “acidic composition analysis”, considering the impact categories overall. Its high level of incidence in all the impact categories depended mainly on the energy-consuming nature of this analysis. The “peroxide content analysis” showed a high amount in the impact category OD due to the quantity and type of chemicals used. Despite this, this analysis was overall considered to be environmentally safer in comparison with the other two. The “tocopherols analysis” showed a balanced distribution of the percentage of responsibility in all the impact categories. The main contribution to its impact assessment derived from the analytical tools (e.g., HPLC), both in term of construction and in terms of energy demand necessary to perform the analysis.

From this scenario where the chemical analyses were energy-consuming, required reagents, and implied a disposal cost for these hazardous substances, it was possible to make a comparison with the optical or non-destructive vis/NIR analyses, which did not require chemicals, laboratory materials, or sample preparation. As for the chemical analyses, the same study had been performed for the vis/NIR spectroscopic analyses, identifying the environmental profile and representing it in Figure 4.

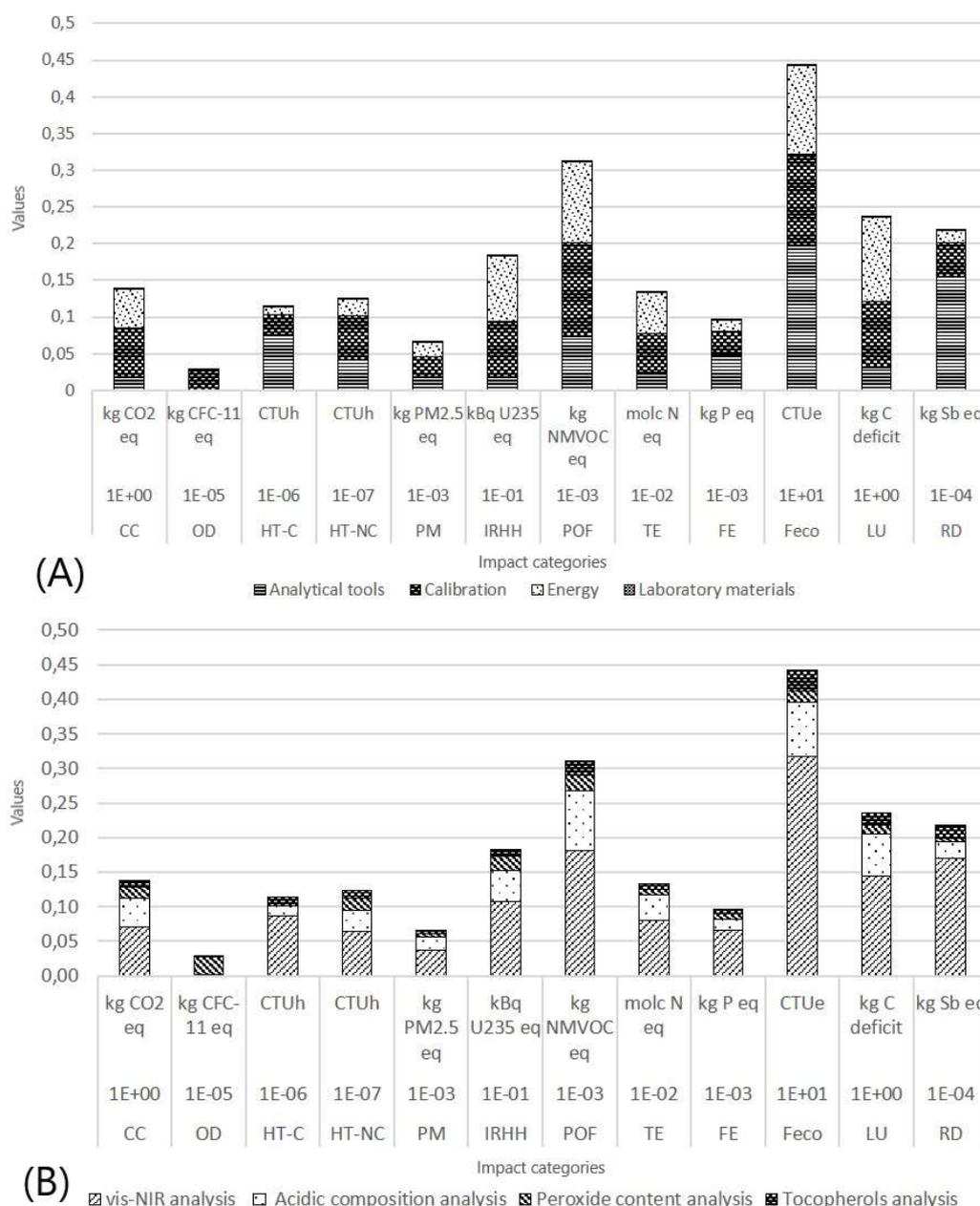


Figure 4. Impact assessment of the vis/NIR analysis with the subdivision of the environmental impacts among the factors (A) and among the type of analysis (optical measurement + calibration analyses; (B)).

Figure 4a reports the environmental impact assessment related to the execution of one optical vis/NIR analysis, dividing the impacts into four factors: (i) “Analytical tools”, (ii) “calibration”, (iii) “energy”, and (iv) “laboratory materials”. All the impact categories were related to the relative unit of measurement, this allowed us to quantify the environmental impact. It was evident that the values on the *y* axis were considerably lower in comparison with that of the chemical analyses.

The “analytical tools” factor, as for the previous scenario, had a high level of incidence due to the extraction of raw materials, like steel and copper, and to the production of the analytical tools (computer and vis/NIR device). The higher amount was attributable to the HT-C, FEco, and RD impact categories showing percentages equal to 62%, 43%, and 68%, respectively.

The calibration showed an impact contribution from 40% (LU, PM) to 98% for the OD impact category. The large variability of this factor and the high level reached in some of the impact categories was due to the impact assessment of the chemical analyses necessary as a reference for the calibration

of the vis/NIR device. The calibration, even if divided between the 20,000 analyses done in 10 years, had a relevant rate. Moreover, even if the energy factor was not a high one, it had a high level of influence in some of the impact categories such as for IRHH and LU where the level reached was equal to 48% for both.

Focusing the attention on the type of analyses (Figure 4b), the execution of the optical analysis intended as simple spectra acquisition was the major operation responsible of all the impacts, showing a medium impact contribution equal to 58%, which went from 3% for the OD impact category to 78% for the RD impact category. This was due to the construction of the analytical tools (vis/NIR device and the computer) and the energy demanded to perform the optical analysis. The calibration activity also represents a relevant part of the overall impact. Figure 4b shows the distribution of the impacts of the pool of three chemical analyses considered as the reference for model calibration. As expected, high-impact chemical analyses were proportionally reflected in the impact of calibration for that specific parameter.

3.1. Comparison of the Two Realities

The aim of the study was to compare the pool of three chemical analyses (3CA) with the respective one optical vis/NIR analysis (1OA) used to predict the three parameters crucial for olive oil analysis and to identify the safer option for the environment. Table 6 reports the values for all the impact categories, comparing the two types of analyses that were carried out.

Table 6. Comparison of impact contribution between 3CA and 1OA to estimate three parameters.

Impact Category		Coefficient	Unit	3CA*	1OA*	Ratio (R)
Climate change	CC	1	kg CO ₂ eq	5.82	0.14	42.20
Ozone depletion	OD	1 × 10 ⁻⁵	kg CFC-11 eq	2.25	0.03	83.22
Human toxicity, cancer effects	HT-C	1 × 10 ⁻⁶	CTUh	2.33	0.11	20.53
Human toxicity, non-cancer effects	HT-NC	1 × 10 ⁻⁷	CTUh	5.14	0.12	41.60
Particulate matter	PM	1 × 10 ⁻³	kg PM _{2.5} eq	2.41	0.07	36.82
Ionizing radiation HH	IRHH	1 × 10 ⁻¹	kBq U235 eq	6.53	0.18	35.67
Photochemical ozone formation	POF	1 × 10 ⁻³	kg NMVOC eq	11.12	0.31	35.78
Terrestrial eutrophication	TE	1 × 10 ⁻²	molc N eq	4.61	0.13	34.41
Freshwater eutrophication	FE	1 × 10 ⁻³	kg P eq	2.65	0.10	27.61
Freshwater ecotoxicity	FEco	1 × 10	CTUe	10.71	0.44	24.20
Land use	LU	1	kg C deficit	7.77	0.24	32.98
Mineral fossil and renewable resources depletion	RD	1 × 10 ⁻⁴	kg Sb eq	4.12	0.22	18.94

* 3CA: Pool of three chemical analyses; 1OA: one optical analysis.

The last column of Table 6 shows a ratio value (R) for each impact categories calculated as:

$$R = \frac{3CA}{1OA} \quad (2)$$

The ratio showed values between 18 and 83. Considering the wide variability of this value, due to the differences between the analyses, an average value of 36 1OA must be performed to obtain a level of environmental impact equal to the pool of 3CA.

Figure 5 better highlights the divergences between the two types of analyses.

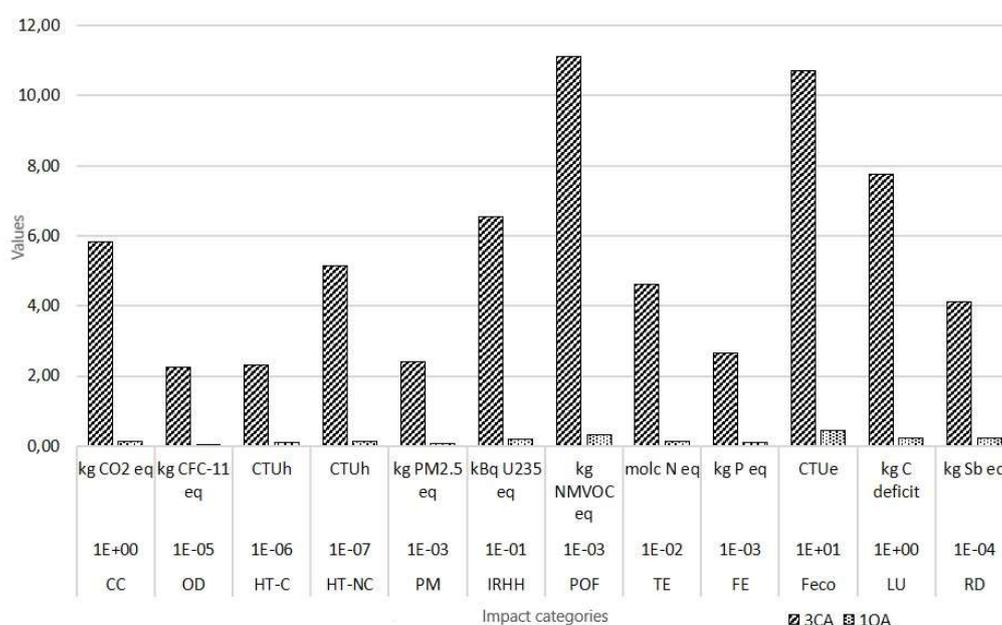


Figure 5. Graphical comparison between the environmental impact of three chemical analyses (3CA) and one optical vis/NIR analysis (10A) to estimate three parameters for olive oil analysis.

The results reported in Figure 5 clearly identify the advantages of performing the analyses using the optical vis/NIR technology. It is a simple and ready to use method [39], which can analyse one sample at a time but estimates different parameters with one single analysis.

With the intention to relate the impact of the analysis method to the olive oil product, Pattara et al. [40] helped to identify a medium value with which correlate the impact of the analyses. Considering (i) an average of 13.32 kg of CO₂ eq per liter of olive oil produced and packaged (from the farm to the disposal), (ii) 5.82 kg of CO₂ eq derived from the chemical analyses performed on olive oil samples, and (iii) 0.14 kg of CO₂ eq derived from the optical analyses, this shows the high importance of the size of the chosen sample of olive oil. If the sample analyzed refers only to one liter, the chemical analyses represent 30% of the whole olive oil production impact, while the optical methods represent only 1%. For commercial and economic reasons, the analyses were normally carried out on samples that represent quantities of the product that are considerably higher than 1 L, for example, considering a sample analyzed that is representative for 1,000 L, the chemical analyses will have a percentage of impact equal to 0.04% of the total, while the optical one is only 0.0001%.

3.2. Sensitivity Analysis

A sensitivity analysis was carried out to evaluate how sensitive the results were to the variation in energy mix parameters, which could be assumed as the potential most affecting variable. Considering the three major EU olive oil producers (Spain, Italy, and Greece) [1], relative country mixes were varied as to the energy input. Moreover, a variation of the Italian country mix was performed to hypothesize that 100% of the energy comes from renewable resources such as photovoltaic panels. According to the variation of the country energy mix, a mean value and standard deviation were found and reported in Table 7.

Table 7. Variation in energy country mix input and its sensitivity between 3CA and 1OA to estimate three parameters.

Impact Category	Unit	Coefficient	Greece Country Mix		Italy Country Mix		Spain Country Mix		100% Renewable		Mean ± SD **	
			3CA *	1OA *	3CA *	1OA *	3CA *	1OA *	3CA *	1OA *	3CA *	1OA *
CC	kg CO ₂ eq	1	8.44	0.19	5.82	0.14	5.33	0.13	3.86	0.10	5.00 ± 0.83	0.12 ± 0.02
OD	kg CFC-11 eq	1 × 10 ⁻⁵	2.25	0.03	2.25	0.03	2.25	0.03	2.23	0.03	2.25 ± 0.01	0.03 ± 0.00
HT-C	CTUh	1 × 10 ⁻⁶	5.27	0.18	2.33	0.11	2.52	0.12	2.42	0.12	2.42 ± 0.08	0.12 ± 0.00
HT-NC	CTUh	1 × 10 ⁻⁷	14.07	0.32	5.14	0.12	5.54	0.13	4.96	0.12	5.22 ± 0.24	0.13 ± 0.01
PM	kg PM _{2.5} eq	1 × 10 ⁻³	5.01	0.12	2.41	0.07	2.86	0.08	2.00	0.06	2.42 ± 0.35	0.07 ± 0.01
IRHH	kBq U235 eq	1 × 10 ⁻¹	4.50	0.14	6.53	0.18	14.96	0.36	2.99	0.11	8.16 ± 5.02	0.22 ± 0.11
POF	kg NMVOC eq	1 × 10 ⁻³	14.77	0.39	11.12	0.31	14.04	0.37	7.89	0.24	11.02 ± 2.52	0.31 ± 0.05
TE	molc N eq	1 × 10 ⁻²	4.90	0.14	4.61	0.13	5.03	0.14	2.61	0.09	4.08 ± 1.06	0.12 ± 0.02
FE	kg P eq	1 × 10 ⁻³	15.48	0.37	2.65	0.10	2.84	0.10	2.33	0.09	2.61 ± 0.21	0.10 ± 0.00
FEco	CTUe	1 × 10	19.38	0.63	10.71	0.44	10.97	0.45	11.62	0.46	11.10 ± 0.38	0.45 ± 0.01
LU	kg C deficit	1	4.02	0.15	7.77	0.24	5.46	0.19	18.43	0.46	10.55 ± 5.65	0.30 ± 0.12
RD	kg Sb eq	1 × 10 ⁻⁴	3.94	0.21	4.12	0.22	3.94	0.21	5.95	0.26	4.66 ± 0.91	0.23 ± 0.02

** SD: Standard deviation; * 3CA: Pool of three chemical analyses; * 1OA: one optical analysis.

Considering the results obtained, no reasonable variation could be attributed to the changes in the country energy mix. The environmental gap between the two methods in different “country mix scenarios” demonstrated how from the initial value (36 times) no relevant variations were identified (38.7 times in Greece, 36.7 in Spain, and 35.4 in the renewable resources scenario).

4. Conclusions

The results highlight a clear impact disparity between the two methods of analysis. The chemical analyses identified are linked to the energy demand, analytical tools construction, and chemicals production. Even if the chemical analyses have seen the reduction of the chemicals and the energy used during recent years, their impact compared to that of the optical solution was huge. By contrast, the impact of vis/NIR spectroscopy on the environment was due to (i) the production of the analytical tools, (ii) the energy power absorption, and (iii) the calibration procedures. In this scenario, the environmental impact of the optical analyses implies that a part of it is derived from the chemical analyses used as calibration references.

From a laboratory point of view, hypothesizing to substitute the chemical analyses with the optical one [31], this operation can reduce largely the impact related to the execution of the different analyses saving 11,360 kg CO₂ eq per year per laboratory. A comparison between chemical and optical methods showed an impact average gap of 36 times. This number could be increased by (i) increasing the number of samples analyzed during the life cycle of the vis/NIR device and (ii) implementing predictive models capable of estimating a wider number of parameters simultaneously.

Moreover, the important aspect that must not be neglected is that the optical analyses were performed in less time, without chemicals, and with less waste to dispose of, but refer to a prediction of the parameter. The chemical analyses gave the actual values but required analysis of the samples in replicate and used chemicals and energy in high quantity. In some cases, a laboratory needs both chemical and optical tools, but in view of the rapid evolution of these optical devices, a number of bench top instruments are already available to be used in complete substitution for the chemical methods. Moreover, this trend can only increase during the coming years.

In conclusion, this study can be a starting point to evaluate the environmental benefits of a consolidated method like vis/NIR spectroscopy that can be applied in a wide range of sectors: e.g., chemical, pharmaceutical, and agri-food. Moreover, the implementation of this green technology in the food chain can be useful and contribute to an eco-design approach to a process such as the olive oil production chain.

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