

Sensitivity of leaf chlorophyll empirical estimators obtained at Sentinel-2 spectral resolution for different canopy structures

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Abstract A comparison of the sensitivity of canopy scale estimators of leaf chlorophyll, obtainable with Sentinel-2 spectral resolution, to soil, canopy and leaf mesophyll factors, was addressed. The analysis of a synthetic dataset, generated simulating the reflectance in the 1–4 LAI range of canopies for the main general classes of leaf inclination (i.e. erectophile, plagiophile, spherical, planophile and extremophile) and for different soil types was used for such a purpose. The synthetic dataset was obtained using the PROSPECT5-4SAIL model in the direct mode with a large variety of soil backgrounds. Additionally an experimental dataset including airborne hyperspectral data gathered during ESA (European Space Agency) campaigns SPARC and AGRISAR, was employed to simulate Sentinel-2 spectral and spatial resolution, to confirm model results. Analysis of the synthetic and experimental datasets indicated that: (i) the CVI (Chlorophyll Vegetation Index), relying only on visible and NIR (Near Infra-Red) bands and obtainable at 10 m spatial resolution, can be used as leaf chlorophyll estimator, at growth stages suitable for nitrogen fertilizer topdressings, for all canopy structures except for erectophile canopies; (ii) better results can be obtained by using different indices for different leaf architectures, with TCI/OSAVI (Triangular Chlorophyll Index/Optimized Soil Adjusted Vegetation Index) performing better for erectophile canopies, whereas MTCI (MERIS Terrestrial Chlorophyll Index) provides better results for planophile canopies, despite the fact that these indices require bands obtainable at 20 m spatial resolution from Sentinel-2 data.

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Introduction

Leaf chlorophyll density, i.e. the amount of chlorophyll *a* and *b* per unit leaf area, is sensitive to soil nitrogen availability, making it probably the most effective biophysical indicator of nitrogen deficiency (Daughtry et al. 2000). Handheld leaf chlorophyll meters, such as SPAD-502 (Minolta Ltd., Japan) are being used for in-season optimum nitrogen rate determination in traditional (i.e. not spatially variable) nitrogen applications (Samborski et al. 2009; Solari et al. 2010). Because of the spatial variability of soil nitrogen, however, there is a requirement for spatialized data, whose collection by hand-held chlorophyll meters is not feasible. Hence, proximal and remote optical multi-spectral sensors (i.e. on-the-go active sensors mounted on nitrogen fertilizer applicators—Samborski et al. 2009; Solari et al. 2010), and airborne or space-borne imaging spectrometers (Baret et al. 2007a) are used to provide timely leaf chlorophyll spatial estimations from canopy reflectance for in-season site-specific nitrogen prescriptions. The Sentinel-2 (S2) constellation of the European Space Agency, of which the first satellite was launched in June 2015, is expected to represent a breakthrough for the exploitation of earth observation data in precision agriculture applications. Freely available S2 data include three visible and one NIR (Near Infra-Red) spectral bands at 10 m spatial resolution and three spectral bands in the red-edge at 20 m resolution. Given these characteristics, Sentinel-2 data can be expected to improve significantly the availability of accurate leaf chlorophyll density spatial estimates at the field scale for variable rate nitrogen fertilization.

The estimation of leaf chlorophyll from remote sensing data can be attempted by using either physically based approaches, relying on the inversion of canopy reflectance models, or by using empirical approaches based on vegetation indices (Vegetation Indices—VIs).

Although the former approaches aim to be of more general applicability and transferability, they have a number of shortcomings. When inversion techniques are used for the estimation of canopy reflectance model parameters, the radiometric information is not sufficient to identify a unique solution: different sets of model input parameters may yield similar output (i.e. spectra), presenting what is called an identifiability problem (Varella et al. 2010). Hence, model inversion is hampered by the ill-posed nature of the inversion process, which leads to unstable inversion results due to the counterbalance of some parameters (Bacour et al. 2002a). For this reason, temporal (Koetz et al. 2005) or spatial (Atzberger 2004) constraints are required. Additionally, model inversion is too computationally intensive for operational applications, therefore pre-computed solutions are provided by means of look-up-tables (Casa and Jones 2005) or neural networks (Baret et al. 2007b).

Conversely, the use of empirical estimators (Vegetation Indices—VIs) has proved to be desirable for operational mapping of leaf chlorophyll density due to their simplicity. Sentinel-2 Multi Spectral Imager (MSI) data can be used to calculate indices obtainable from visible and NIR bands at 10 m spatial resolution and indices requiring narrow bands in the red-edge at 20 m resolution (Table 1).

Several VIs using red-edge bands have proved, for different crops, to be sensitive to leaf chlorophyll density at the canopy scale (Daughtry et al. 2000; Dash and Curran 2001;

Table 1 Spectral bands for the SENTINEL-2 Multi Spectral Imager (MSI) sensor

Band number	Central wavelength (nm)	Bandwidth (nm)	Spatial resolution (m)	Employed for ^a
1	443	20	60	
2	490	65	10	
3	560	35	10	ρ_{green} , ρ_{550}
4	665	30	10	ρ_{red} , ρ_{665} , ρ_{670} , ρ_{680}
5	705	15	20	ρ_{700} , ρ_{705} , ρ_{710}
6	740	15	20	ρ_{750} , ρ_{740} , $\rho_{red\ edge}$
7	783	20	20	ρ_{783} , ρ_{800}
8	842	115	10	ρ_{NIR}
8a	865	20	20	
9	945	20	60	
10	1380	30	60	
11	1610	90	20	
12	2190	180	20	

^a Employed to calculate vegetation indices: see Table 2

Haboudane et al. 2008). A few VIs not requiring bands in the red-edge, based on the green and NIR reflectance (Gitelson et al. 1996, 2005) or also including reflectance in the red (Vincini et al. 2008), have been proposed with the same objective.

However, little agreement exists on which VI is the best leaf chlorophyll density estimator at the canopy scale for low LAI (Leaf Area Index) values (Haboudane et al. 2008; Vincini and Frazzi 2011). The reliability of using empirical VIs for such a situation is limited by the fact that they can be influenced by site- and scene-specific conditions, especially soil background, when up-scaled from leaf to canopy level. More extensive studies are therefore required in order to assess the sensitivity of the most widely used indices to leaf chlorophyll and to the confounding factors at the initial stages of crop growth. Whereas extensive experimental datasets can help to identify the best indices, they are however influenced by the specific soil-crop-illumination conditions, as well as by the experimental error, under which they were collected. Models such as the popular coupled leaf and canopy PROSPECT + SAILH (Jacquemoud et al. 1995, 2000) can supplement the information that may be obtained from experimental datasets, by simulating a wider combination of soil, crop and illumination conditions. When used for such a purpose, i.e. run in the direct mode, they are valuable tools for sensitivity analysis studies (Vincini et al. 2014) and the issue of identifiability is not relevant. In fact, the purpose is not to establish a univocal link between parameters (e.g. chlorophyll) and outputs (VIs), but rather to identify the indices that have the highest sensitivity to leaf chlorophyll and the lowest sensitivity to confounding factors such as background soil reflectance or canopy structure.

The latest version of the coupled model PROSPECT5-4SAIL (Verhoef et al. 2007; Féret et al. 2008) has introduced significant modifications in modelling canopy structure (4SAIL) and leaf biochemical components (PROSPECT5). Due to the fact that in-season nitrogen applications are often carried out at early growth stages, such spectral indicators should be sensitive to leaf chlorophyll density before canopy closure (i.e. for low LAI values), when soil spectral behavior largely affects canopy spectral signatures. One primary variable influencing crop spectral behavior especially at early phenological stages is the angular distribution of leaves. While, in previous SAIL versions, a single parameter, the average

leaf angle (ALA) was used to model the leaf inclination distribution function (LIDF), 4SAIL uses the function proposed by Verhoef (1997) with two parameters, controlling the average leaf inclination and the distribution bimodality. Erectophile, plagiophile, spherical and planophile are the most commonly reported general classes of leaf inclination (de Wit 1965; Campbell 1990; Verhoef 1997). As the name suggests, erectophile canopies possess mostly erect leaves whereas a planophile canopy possesses mostly horizontal leaves. The spherical distribution shows a relative frequency of inclinations similar to the relative frequency of surface elements of a sphere. In a plagiophile canopy, leaves are most frequent at an oblique inclination and extremophile leaves are least frequent at oblique inclinations. It should be noted that different crop genotypes as well as development stages can have considerably different angular distribution of leaves within the same species.

Additionally, 4SAIL calculates the directional reflectance by taking into account the direct and diffuse components of the incident solar radiation as proposed by François et al. (2002).

Findings obtained from previous works (Vincini and Frazzi 2013; Vincini et al. 2014) conducted using older versions of the coupled leaf and canopy reflectance model indicate that at early phenological stages (i.e. before canopy closure) the Triangular Chlorophyll Index/Optimized Soil Adjusted VI ratio (TCI/OSAVI, Haboudane et al. 2008) and the MTCI (MERIS Terrestrial Chlorophyll Index, Dash and Curran 2001) indices, both obtainable at 20 m spatial resolution from S2 data, and the Chlorophyll Vegetation Index (CVI, Vincini et al. 2008), obtainable with 10 m S2 data, are very accurate leaf chlorophyll estimators. In particular these results indicated that:

- (i) The TCI/OSAVI index, is the best leaf chlorophyll estimator for erectophile canopies among VIs obtainable from 20 m Sentinel-2 red-edge bands;
- (ii) For planophile crops, the TCI/OSAVI or the MTCI indices are the best leaf chlorophyll estimator among VIs obtainable from 20 m Sentinel-2 red-edge bands depending on leaf structure (i.e. crop, genotype);
- (iii) The CVI index, obtainable at 10 m spatial resolution from Sentinel-2 visible and NIR (Near Infra Red) bands, can be used as a leaf chlorophyll estimator both for planophile crops and winter wheat in most soil conditions and outperforms best red-edge estimators, obtainable only at 20 m resolution, for dark/wet soils.

Canopy reflectance models can accurately simulate the spectral behavior at early phenological stages of crops characterized by different angular distribution of leaves, provided they are correctly parameterized and that the assumptions on which they are based are met. The present work addresses a comparison of the sensitivity and portability of leaf chlorophyll estimators obtainable at Sentinel-2 spectral resolution, at growth stages suitable for nitrogen fertilization, with different crops/soil/illumination conditions. The comparison is carried out using both an extensive experimental dataset gathered during ESA (European Space Agency) campaigns and PROSPECT5-4SAIL synthetic reflectance of canopies for different general classes of leaf inclination (i.e. erectophile, plagiophile, spherical, planophile and extremophile) in the 1–4 LAI range.

Materials and methods

Synthetic dataset

The PROSPECT5-4SAIL leaf and canopy coupled reflectance model (Verhoef et al. 2007; Féret et al. 2008) was used in the direct mode in order to obtain a synthetic data set

representing reflectance of canopies for main general classes of leaf inclination (i.e. erectophile, plagiophile, spherical, planophile and extremophile) at growth stages suitable for spring nitrogen dressing (i.e. in the LAI range 1 to 4) in a wide range of soil conditions.

The model output consists of canopy reflectance spectra in the range of 400–2400 nm, which were resampled to the spectral wavebands of the Sentinel-2 MSI sensor. The soil reflectance database (Daughtry et al. 1997) used as model input included the spectral reflectances of six different soils representing a large spectral variability. For each soil characterized by a large reflectance variability between wet and dry conditions (Othello, Cecil, Portneuf and Cordorus in Tables 2, 3, 4), two spectral reflectances were used, representing wet and dry soil conditions (Fig. 1). For soils with little variability in soil reflectance related to soil moisture (Barnes and Houston Black Clay in Tables 2, 3, 4), a single spectral reflectance was used, representing intermediate soil moisture conditions.

The acquisition geometries considered in the synthetic database included only nadir observation (i.e., with zero view zenith angle) and two solar zenith angles (20° and 40°). Leaf chlorophyll (a + b) density varied from 23 (i.e., leaf chlorosis) to 68 μg·cm⁻², with 3.0-μg·cm⁻² increments. Given the sensitivity of simulated reflectance in the NIR (Bacour et al., 2002b) to the mesophyll structure index value (N), in the present work three N values (N = 1 i.e. lowest value accepted by the model, N = 1.5 and N = 2) were used. These values represent the N leaf structure parameter range typically used in the literature for different crops. Other PROSPECT input parameters were set to suggested typical values (carotenoid content 8 μg·cm⁻², brown pigment content 0 arbitrary units, equivalent water thickness 0.01 cm and leaf mass per area 0.009 g·cm⁻²). The decision to keep these latter parameters constant was motivated by the results of sensitivity analysis studies on the PROSPECT + SAIL model (Jacquemoud et al. 2009) which revealed that in the visible and NIR part of the spectrum they have a negligible influence on canopy spectra.

The two-parameter (*a*, *b*) linear combination of trigonometric functions proposed by Verhoef (1997) is used in 4SAIL (Verhoef et al. 2007) to model the leaf inclination distribution function (LIDF), where *a* and *b* are the two parameters, the former controlling

Table 2 Equations and Sentinel-2 bands used for VI employed in this paper

Index	Formula	Suitable S2 bands	S2 resolution
NDVI	$(\rho_{NIR} - \rho_{red}) / (\rho_{NIR} + \rho_{red})$	B4, B8	10 m
Green NDVI	$(\rho_{NIR} - \rho_{green}) / (\rho_{NIR} + \rho_{green})$	B3, B8	10 m
Green SR (CI _{green}) ^a	$(\rho_{NIR} / \rho_{green})$	B3, B8	10 m
CVI	$(\rho_{NIR} / \rho_{green}) \cdot (\rho_{red} / \rho_{green})$	B3, B4, B8	10 m
MTCI	$(\rho_{750} - \rho_{710}) / (\rho_{710} - \rho_{680})$	B4, B5, B6	20 m
CI _{red-edge}	$(\rho_{NIR} / \rho_{red-edge}) - 1$	B6, B8	20 m
TCI/OSAVI ^b	$(1.2 \cdot (\rho_{700} - \rho_{550}) - 1.5 \cdot (\rho_{670} - \rho_{550}) \cdot \sqrt{\rho_{700} / \rho_{670}}) / \text{OSAVI}$	B3, B4, B5	20 m
REP _{S2}	$\rho_{705} + 35 \{ [0.5 \cdot (\rho_{783} - \rho_{665}) - \rho_{705}] / (\rho_{740} - \rho_{705}) \}$	B4, B5, B6, B7	20 m

^a The Chlorophyll Index (green) has a slightly different formula: $(\rho_{NIR} / \rho_{green}) - 1$

^b $\text{OSAVI} = (\rho_{800} - \rho_{670}) / (\rho_{800} + \rho_{670} + 0.16)$

Table 3 Coefficient of determination (R^2) values of VI versus leaf chlorophyll ($a + b$) content for erectophile canopies ($LIDF_a = -1$, $LIDF_b = 0$) data synthesized by different input parameters; – maximum R^2 value in bold

VI	Soil	sun zenith 20°										sun zenith 40°																
		Othello		Barnes		Cecil		H.B.C.		Portneuf		Cordorus		Othello		Barnes		Cecil		H.B.C.		Portneuf		Cordorus				
		dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a	dry	wet	int. ^a
N = 1	Green NDVI	0.05	0.12	0.17	0.07	0.12	0.15	0.06	0.11	0.05	0.09	0.07	0.16	0.21	0.08	0.14	0.19	0.07	0.14	0.19	0.07	0.14	0.06	0.12	0.14	0.06	0.12	
	Green SR	0.07	0.15	0.19	0.08	0.14	0.18	0.08	0.14	0.07	0.12	0.10	0.20	0.25	0.12	0.18	0.25	0.11	0.18	0.25	0.11	0.18	0.10	0.16	0.11	0.18	0.10	0.16
	CVI	0.22	0.46	0.56	0.28	0.46	0.52	0.25	0.44	0.21	0.37	0.32	0.62	0.71	0.41	0.62	0.66	0.36	0.58	0.66	0.36	0.58	0.31	0.52	0.36	0.58	0.31	0.52
	MTCI	0.50	0.52	0.58	0.50	0.46	0.64	0.53	0.52	0.50	0.49	0.53	0.56	0.62	0.52	0.52	0.67	0.56	0.56	0.67	0.56	0.56	0.52	0.52	0.56	0.52	0.52	0.53
	CI red-edge	0.35	0.48	0.50	0.31	0.36	0.50	0.35	0.41	0.31	0.37	0.38	0.52	0.55	0.34	0.40	0.55	0.38	0.45	0.55	0.38	0.45	0.35	0.42	0.38	0.45	0.35	0.42
N = 1.5	TCI/OSAVI	0.69	0.90	0.92	0.85	0.90	0.92	0.77	0.90	0.67	0.86	0.72	0.92	0.92	0.83	0.92	0.92	0.79	0.92	0.92	0.79	0.92	0.67	0.88	0.83	0.92	0.67	0.88
	REP	0.69	0.76	0.76	0.59	0.61	0.77	0.67	0.69	0.61	0.66	0.69	0.76	0.76	0.59	0.62	0.76	0.67	0.69	0.76	0.67	0.69	0.61	0.67	0.67	0.69	0.61	0.67
	Green NDVI	0.06	0.17	0.22	0.08	0.15	0.20	0.07	0.14	0.06	0.12	0.07	0.19	0.25	0.10	0.18	0.24	0.08	0.17	0.24	0.08	0.17	0.07	0.14	0.10	0.17	0.07	0.14
	Green SR	0.08	0.19	0.25	0.10	0.18	0.23	0.10	0.17	0.08	0.14	0.11	0.24	0.29	0.14	0.22	0.28	0.13	0.21	0.28	0.13	0.21	0.11	0.18	0.13	0.21	0.11	0.18
	CVI	0.27	0.58	0.67	0.35	0.58	0.64	0.31	0.53	0.26	0.46	0.37	0.71	0.79	0.48	0.71	0.74	0.42	0.66	0.74	0.42	0.66	0.36	0.59	0.42	0.66	0.36	0.59
N = 2	MTCI	0.58	0.58	0.64	0.56	0.53	0.69	0.59	0.58	0.56	0.55	0.59	0.61	0.66	0.58	0.56	0.71	0.61	0.61	0.71	0.61	0.61	0.58	0.58	0.61	0.61	0.58	0.58
	CI red-edge	0.36	0.49	0.52	0.32	0.37	0.52	0.36	0.42	0.32	0.40	0.40	0.53	0.55	0.35	0.41	0.55	0.38	0.46	0.55	0.38	0.46	0.36	0.42	0.38	0.46	0.36	0.42
	TCI/OSAVI	0.77	0.94	0.92	0.88	0.94	0.92	0.83	0.94	0.74	0.90	0.77	0.92	0.92	0.86	0.94	0.92	0.85	0.94	0.92	0.85	0.94	0.72	0.92	0.86	0.94	0.72	0.92
	REP	0.72	0.77	0.77	0.62	0.64	0.77	0.72	0.72	0.64	0.71	0.72	0.76	0.76	0.62	0.66	0.76	0.71	0.71	0.76	0.71	0.71	0.64	0.71	0.71	0.71	0.64	0.71
	Green NDVI	0.07	0.20	0.26	0.10	0.18	0.24	0.08	0.17	0.07	0.14	0.08	0.22	0.29	0.11	0.20	0.27	0.10	0.19	0.27	0.10	0.19	0.08	0.16	0.10	0.19	0.08	0.16
N = 2	Green SR	0.10	0.22	0.28	0.12	0.21	0.27	0.11	0.20	0.09	0.17	0.12	0.26	0.32	0.15	0.24	0.30	0.14	0.24	0.30	0.14	0.24	0.12	0.20	0.14	0.24	0.12	0.20
	CVI	0.31	0.67	0.77	0.41	0.67	0.72	0.37	0.62	0.30	0.55	0.42	0.77	0.86	0.53	0.79	0.81	0.48	0.74	0.81	0.48	0.74	0.40	0.67	0.48	0.74	0.40	0.67
	MTCI	0.61	0.61	0.66	0.59	0.56	0.71	0.62	0.59	0.59	0.58	0.62	0.62	0.67	0.61	0.58	0.71	0.64	0.62	0.71	0.64	0.62	0.61	0.59	0.64	0.62	0.61	0.59
	CI red-edge	0.37	0.50	0.53	0.32	0.38	0.53	0.37	0.44	0.34	0.41	0.40	0.53	0.56	0.36	0.42	0.56	0.40	0.48	0.56	0.40	0.48	0.36	0.44	0.40	0.48	0.36	0.44
	TCI/OSAVI	0.81	0.94	0.92	0.92	0.94	0.92	0.86	0.94	0.77	0.94	0.81	0.94	0.90	0.88	0.94	0.92	0.86	0.94	0.92	0.86	0.94	0.76	0.94	0.86	0.94	0.76	0.94
REP	0.74	0.79	0.77	0.64	0.66	0.77	0.74	0.72	0.66	0.72	0.72	0.76	0.76	0.64	0.66	0.76	0.72	0.71	0.76	0.72	0.71	0.66	0.71	0.72	0.71	0.66	0.71	

^a Intermediate soil moisture

Table 4 Coefficient of determination (R^2) values of VI vs. leaf chlorophyll ($a + b$) content for “spherical” canopies ($LIDF_a = -0.35$, $LIDF_b = -0.15$) data synthesized by different input parameters;— maximum R^2 value in bold

VI	Soil	sun zenith 20°										sun zenith 40°														
		Othello		Barnes		Cecil		H.B.C.		Portneuf		Cordorus		Othello		Barnes		Cecil		H.B.C.		Portneuf		Cordorus		
		dry	wet	int.	int.	dry	wet	int.	int.	dry	wet	dry	wet	dry	wet	int.	int.	dry	wet	dry	wet	int.	int.	dry	wet	dry
N = 1	Green NDVI	0.18	0.41	0.49	0.23	0.38	0.46	0.20	0.37	0.17	0.31	0.20	0.44	0.52	0.26	0.41	0.50	0.23	0.40	0.19	0.35	0.23	0.40	0.19	0.35	
	Green SR	0.25	0.44	0.50	0.29	0.41	0.49	0.27	0.41	0.24	0.36	0.28	0.46	0.53	0.32	0.45	0.52	0.31	0.44	0.27	0.40	0.31	0.44	0.27	0.40	
	CVI	0.62	0.85	0.86	0.77	0.90	0.83	0.67	0.85	0.62	0.81	0.69	0.88	0.88	0.83	0.92	0.86	0.74	0.86	0.69	0.86	0.74	0.86	0.69	0.86	
	MTCI	0.69	0.76	0.79	0.67	0.71	0.83	0.71	0.74	0.66	0.71	0.71	0.77	0.81	0.69	0.72	0.83	0.72	0.76	0.69	0.72	0.72	0.76	0.69	0.72	
	CI red-edge	0.58	0.69	0.69	0.50	0.58	0.69	0.56	0.64	0.52	0.61	0.59	0.69	0.69	0.53	0.61	0.69	0.59	0.64	0.53	0.62	0.59	0.64	0.53	0.62	
N = 1.5	TCI/OSAVI	0.90	0.90	0.88	0.92	0.90	0.90	0.92	0.90	0.88	0.92	0.90	0.90	0.90	0.92	0.90	0.90	0.92	0.90	0.88	0.92	0.90	0.92	0.90	0.88	0.92
	REP	0.77	0.81	0.81	0.71	0.74	0.81	0.76	0.77	0.72	0.77	0.77	0.81	0.81	0.71	0.76	0.81	0.76	0.77	0.72	0.77	0.76	0.77	0.72	0.77	
	Green NDVI	0.26	0.53	0.61	0.34	0.50	0.58	0.29	0.49	0.25	0.44	0.28	0.55	0.62	0.36	0.52	0.59	0.31	0.50	0.27	0.45	0.31	0.50	0.27	0.45	
	Green SR	0.32	0.53	0.59	0.38	0.52	0.58	0.35	0.50	0.31	0.46	0.35	0.55	0.61	0.41	0.53	0.61	0.38	0.53	0.34	0.48	0.38	0.53	0.34	0.48	
	CVI	0.79	0.94	0.94	0.90	0.94	0.92	0.85	0.94	0.79	0.92	0.83	0.94	0.94	0.90	0.94	0.92	0.86	0.94	0.83	0.94	0.86	0.94	0.83	0.94	
N = 2	MTCI	0.79	0.81	0.83	0.77	0.79	0.85	0.81	0.81	0.77	0.79	0.79	0.81	0.83	0.79	0.79	0.85	0.81	0.81	0.79	0.79	0.81	0.81	0.79	0.79	
	CI red-edge	0.61	0.69	0.69	0.53	0.61	0.69	0.59	0.64	0.55	0.62	0.62	0.71	0.69	0.55	0.62	0.69	0.61	0.66	0.56	0.64	0.61	0.66	0.56	0.64	
	TCI/OSAVI	0.94	0.90	0.88	0.94	0.90	0.90	0.94	0.90	0.94	0.90	0.94	0.90	0.90	0.92	0.90	0.90	0.94	0.90	0.94	0.90	0.94	0.90	0.94	0.92	
	REP	0.81	0.81	0.81	0.76	0.77	0.81	0.81	0.79	0.77	0.79	0.81	0.81	0.81	0.76	0.77	0.79	0.79	0.79	0.77	0.79	0.79	0.79	0.77	0.79	
	Green NDVI	0.31	0.59	0.66	0.41	0.58	0.64	0.36	0.56	0.30	0.50	0.34	0.61	0.66	0.42	0.59	0.64	0.37	0.58	0.32	0.52	0.37	0.58	0.32	0.52	
N = 2	Green SR	0.37	0.59	0.64	0.44	0.58	0.64	0.40	0.56	0.36	0.52	0.40	0.61	0.66	0.46	0.59	0.64	0.42	0.58	0.38	0.53	0.42	0.58	0.38	0.53	
	CVI	0.88	0.96	0.98	0.90	0.90	0.96	0.92	0.96	0.88	0.94	0.90	0.96	0.98	0.90	0.90	0.96	0.92	0.96	0.90	0.94	0.92	0.96	0.90	0.94	
	MTCI	0.83	0.83	0.85	0.83	0.81	0.85	0.85	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.81	0.85	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	
	CI red-edge	0.62	0.71	0.69	0.55	0.62	0.67	0.61	0.66	0.56	0.64	0.64	0.71	0.69	0.56	0.62	0.69	0.62	0.66	0.58	0.66	0.62	0.66	0.58	0.66	
	TCI/OSAVI	0.94	0.88	0.88	0.92	0.86	0.88	0.92	0.88	0.94	0.88	0.94	0.88	0.90	0.92	0.88	0.90	0.92	0.88	0.94	0.90	0.92	0.88	0.94	0.90	
REP	0.83	0.81	0.81	0.79	0.79	0.79	0.81	0.79	0.81	0.81	0.83	0.81	0.79	0.77	0.77	0.79	0.81	0.79	0.79	0.81	0.79	0.81	0.79	0.79		

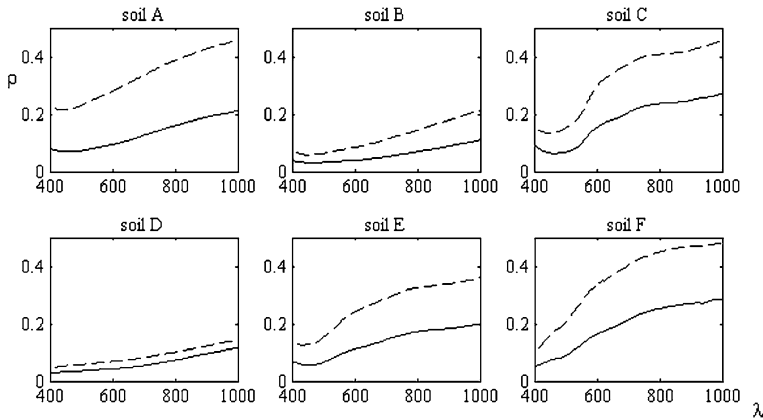


Fig. 1 Spectral reflectance of wet (*solid lines*) and dry (*dashed lines*) soils Othello (**a**), Barnes (**b**), Cecil (**c**), Houston Black Clay (**d**), Portneuf (**e**), Cordorus (**f**) (From Vincini et al. 2008)

the average leaf inclination and the latter the distribution bimodality. Canopies for leaf inclination general classes were simulated using typical values for the class of the two-parameter leaf inclination distribution function (i.e. erectophile $a = -1$ $b = 0$, spherical $a = -0.35$ $b = -0.15$, planophile $a = 1$ $b = 0$, plagiophile $a = 0$ $b = -1$ and extremophile $a = 0$ $b = 1$) and a 1–4 LAI range with increments of 0.2. The hot-spot size parameter was set to 0.1 for erectophile and spherical canopies, 0.25 for plagiophile and extremophile and 0.5 for planophile. This parameter depends on the relative size of the leaves of the crop in relation to their height and has an impact only when remote sensing measurements are acquired near the principal plane. Baret et al. (2010) showed that, in most crops, the hot-spot parameter values are between 0.05 and 1, with smaller values for erectophile crops having smaller leaves and larger values for planophile crops with larger leaves.

The resulting synthetic dataset included simulated soil-canopy spectral reflectance data for 76,800 different soil/leaf/canopy/illumination conditions (5 leaf inclination classes, 10 soil types and moisture levels, three N leaf structural parameter values, 16 LAI values, 16 leaf chlorophyll densities 2 sun zenith angles).

Indices considered in the present work included only VIs whose originally-proposed wavelengths could be roughly matched by S2 center wavebands at high spatial resolution (i.e. 10–20 m). The VIs considered included those incorporating green reflectance, specifically proposed as leaf chlorophyll estimators (i.e. Green NDVI—Gitelson et al., 1996, Green SR—Green Simple Ratio—or its modification CI_{green} , the chlorophyll index based on the green reflectance—Gitelson et al. 2005 and CVI—chlorophyll vegetation index—Vincini et al. 2008). Red-edge indices included only VIs specifically indicated as the best leaf chlorophyll estimators at the canopy scale by recent literature or in-field radiometric experiments conducted using Sentinel-2 spectral resolution (i.e. TCI/OSAVI—Haboudane et al. 2008, REP—Red Edge Position obtained from S2 bands by the linear interpolation method—Vincini et al. 2014, MTCI—MERIS terrestrial chlorophyll index—Dash and Curran 2001 and $CI_{red-edge}$ —Chlorophyll Index based on red-edge reflectance, Gitelson et al. 2006). In Table 1, the equations and Sentinel-2 bands used for the calculation of the VIs tested are reported. VIs based on visible-NIR bands and based on red-edge bands were obtained from average synthetic reflectance in spectral ranges corresponding to

S2 bands, the former from the 10 m spatial resolution bands B3, B4 and B8 and the latter from 20 m resolution bands B5, B6 and B7. Sentinel-2 bands with the closest spectral position to VI original wavelengths were selected for VI calculation.

Given the little deviation from linearity in the relationships between the indices tested and chlorophyll (Vincini and Frazzi 2013; Vincini et al. 2014), the R^2 coefficient of determination of linear regressions between VI and leaf chlorophyll density was used to compare the sensitivity of chlorophyll estimators in the 1–4 LAI range for different soil/leaf/canopy/illumination conditions.

Experimental dataset

The experimental dataset included concurrent airborne and ground data acquired during intensive measurement campaigns SPARC-2003, SPARC-2004 and AGRISAR-2006, carried out by several research teams with the support of ESA. Airborne hyperspectral data were used to simulate the spectral and spatial resolution of the Sentinel-2 MSI sensor. The SPARC campaigns were carried out in 2003 and 2004 in Barrax, La Mancha, Spain (30°3' N, 2°6' W, altitude 700 m). In 2003, ground chlorophyll a + b measurements were made on 12–14 July 2003, employing a CCM-200 Chlorophyll Content Meter (Konica Minolta, Marunouchi, Chiyoda-ku, Tokyo, Japan), specifically calibrated during the campaign by means of laboratory analyses of about 100 leaf disk samples, using spectroscopic and HPLC methods (Gandía et al. 2005). For different crops, i.e. maize, sugarbeet, garlic, onion and potato, between 50 and 100 CCM-200 measurements were acquired for each elementary sampling unit (ESU), around a radius of 10 m of a GPS geo-referenced point, on the upper leaves. All measurements carried out in an ESU were averaged and represent the mean leaf chlorophyll value for an area of around 134 m² (i.e. slightly larger than that of a 10 by 10 m pixel as for Sentinel-2 bands 2, 3, 4 and 8). Additionally, leaf area index (LAI) was measured using the Li-Cor LAI-2000 (Li-Cor Inc. Lincoln, NE, USA) in each ESU. On the 12th of July 2003, an airborne acquisition was carried out using the Hymap sensor, which has 126 bands in the range 438–2483 nm, with a bandwidth of about 15 nm. The data were corrected geometrically, radiometrically and atmospherically as described in detail by Alonso and Moreno (2005) and Guanter et al. (2005), providing top of the canopy (TOC) spectral reflectance images with a spatial resolution of 6 by 6 m. Finally the data were resampled spectrally, applying Sentinel-2 spectral response filters (ESA 2015), and spatially to a resolution of 10 by 10 m and 20 by 20 m using a nearest neighbour interpolation.

During the SPARC 2004 campaign, leaf chlorophyll values were acquired on the 15–18 July 2003 using CCM-200 and adopting the same sampling protocol as for SPARC 2003, on the same crops as in 2003 with the addition of alfalfa and sunflower. The airborne acquisition was carried out on the 15th of July 2004 using the AHS 80 Airborne Hyperspectral Scanner, which has 21 bands in the range 455–1622 nm with about 28 nm bandwidth. The data were geometrically, radiometrically and atmospherically corrected (Alonso and Moreno 2005; Guanter et al. 2005) obtaining TOC spectral reflectance images with a spatial resolution of 6 by 6 m. Spectral and spatial resampling according to the Sentinel-2 MSI characteristics were carried out as for SPARC 2003.

The AGRISAR campaign was carried out in the DEMMIN (Durable Environmental Multidisciplinary Monitoring Information Network) test site located in Mecklenburg-Western Pomerania in North-East Germany (53°54' lat. N, 13°10' E, alt. 8 m) between April and August 2006. Leaf chlorophyll content was measured using the Minolta SPAD-502 DL between the 4th and the 6th of July in maize, wheat and sugarbeet adopting the

Table 5 Coefficient of determination (R^2) values of VI versus leaf chlorophyll ($a + b$) content for planophile canopies ($LIDF_a = 1, LIDF_b = 0$) data synthesized by different input parameters;— maximum R^2 value in bold

Soil	sun zenith 20°										sun zenith 40°														
	Othello		Barnes		Cecil		H.B.C.		Portneuf		Cordorus		Othello		Barnes		Cecil		H.B.C.		Portneuf		Cordorus		
	dry	wet	int.	dry	wet	int.	dry	wet	int.	dry	wet	int.	dry	wet	int.	dry	wet	int.	dry	wet	int.	dry	wet	int.	
VI																									
<i>N = 1</i>	<i>Green NDVI</i>	0.18	0.41	0.49	0.23	0.38	0.48	0.20	0.37	0.17	0.31	0.20	0.45	0.53	0.26	0.42	0.52	0.23	0.41	0.19	0.35	0.23	0.41	0.19	0.35
	<i>Green SR</i>	0.23	0.43	0.50	0.28	0.41	0.49	0.26	0.40	0.22	0.35	0.27	0.47	0.55	0.32	0.45	0.53	0.30	0.44	0.26	0.40	0.30	0.44	0.26	0.40
	<i>CVI</i>	0.59	0.84	0.86	0.74	0.88	0.83	0.65	0.83	0.59	0.79	0.67	0.88	0.90	0.81	0.92	0.86	0.72	0.87	0.67	0.85	0.72	0.87	0.67	0.85
	<i>MTCI</i>	0.70	0.77	0.81	0.68	0.72	0.85	0.72	0.76	0.67	0.72	0.72	0.79	0.83	0.71	0.74	0.85	0.74	0.78	0.71	0.74	0.74	0.78	0.71	0.74
	<i>CI red-edge</i>	0.58	0.70	0.71	0.51	0.59	0.71	0.57	0.65	0.52	0.61	0.60	0.71	0.71	0.53	0.61	0.71	0.60	0.66	0.55	0.64	0.60	0.66	0.55	0.64
	<i>TCI/OSAVI</i>	0.89	0.90	0.88	0.91	0.91	0.88	0.91	0.90	0.86	0.92	0.91	0.90	0.88	0.92	0.90	0.88	0.92	0.90	0.88	0.90	0.92	0.90	0.88	0.90
	<i>REP</i>	0.80	0.83	0.83	0.73	0.77	0.83	0.79	0.80	0.74	0.79	0.80	0.83	0.83	0.73	0.77	0.83	0.79	0.80	0.74	0.79	0.79	0.80	0.74	0.79
<i>N = 1.5</i>	<i>Green NDVI</i>	0.26	0.54	0.62	0.34	0.52	0.59	0.30	0.50	0.25	0.44	0.29	0.57	0.64	0.37	0.55	0.62	0.33	0.53	0.27	0.48	0.33	0.53	0.27	0.48
	<i>Green SR</i>	0.31	0.54	0.61	0.37	0.52	0.59	0.34	0.51	0.30	0.46	0.35	0.57	0.64	0.41	0.55	0.62	0.38	0.54	0.34	0.49	0.38	0.54	0.34	0.49
	<i>CVI</i>	0.77	0.94	0.96	0.89	0.95	0.94	0.82	0.94	0.77	0.92	0.82	0.95	0.96	0.91	0.95	0.94	0.87	0.95	0.83	0.94	0.87	0.95	0.83	0.94
	<i>MTCI</i>	0.81	0.84	0.86	0.80	0.81	0.88	0.83	0.83	0.81	0.81	0.82	0.84	0.86	0.81	0.81	0.86	0.83	0.84	0.81	0.83	0.83	0.84	0.81	0.83
	<i>CI red-edge</i>	0.62	0.72	0.71	0.54	0.62	0.71	0.61	0.67	0.55	0.64	0.64	0.72	0.72	0.56	0.64	0.71	0.62	0.68	0.58	0.66	0.62	0.68	0.58	0.66
	<i>TCI/OSAVI</i>	0.94	0.88	0.86	0.93	0.89	0.88	0.93	0.89	0.94	0.90	0.94	0.89	0.88	0.93	0.88	0.88	0.93	0.89	0.94	0.90	0.93	0.89	0.94	0.90
	<i>REP</i>	0.85	0.85	0.83	0.79	0.80	0.83	0.83	0.82	0.81	0.83	0.84	0.84	0.83	0.79	0.80	0.83	0.82	0.82	0.79	0.83	0.82	0.82	0.79	0.83
<i>N = 2</i>	<i>Green NDVI</i>	0.33	0.62	0.69	0.42	0.60	0.66	0.37	0.58	0.31	0.52	0.35	0.63	0.69	0.44	0.62	0.67	0.39	0.60	0.34	0.55	0.39	0.60	0.34	0.55
	<i>Green SR</i>	0.37	0.61	0.67	0.44	0.59	0.66	0.40	0.57	0.35	0.52	0.40	0.63	0.69	0.47	0.61	0.67	0.43	0.60	0.38	0.55	0.43	0.60	0.38	0.55
	<i>CVI</i>	0.88	0.97	0.98	0.92	0.92	0.96	0.91	0.96	0.88	0.94	0.91	0.96	0.98	0.90	0.90	0.96	0.93	0.96	0.90	0.94	0.93	0.96	0.90	0.94
	<i>MTCI</i>	0.86	0.86	0.86	0.86	0.84	0.88	0.87	0.86	0.86	0.85	0.86	0.85	0.86	0.86	0.84	0.88	0.87	0.85	0.86	0.85	0.87	0.85	0.86	0.85
	<i>CI red-edge</i>	0.64	0.72	0.72	0.56	0.64	0.71	0.63	0.68	0.58	0.66	0.66	0.73	0.72	0.58	0.65	0.71	0.64	0.68	0.59	0.67	0.64	0.68	0.59	0.67
	<i>TCI/OSAVI</i>	0.94	0.85	0.85	0.92	0.85	0.85	0.92	0.86	0.94	0.88	0.93	0.87	0.86	0.91	0.86	0.88	0.92	0.87	0.94	0.88	0.92	0.87	0.94	0.88
	<i>REP</i>	0.87	0.85	0.83	0.82	0.82	0.83	0.85	0.83	0.83	0.83	0.85	0.84	0.83	0.81	0.81	0.83	0.84	0.82	0.83	0.83	0.84	0.82	0.83	0.83

same protocol as for SPARC. In order to calibrate the SPAD-502 chlorophyll meter, 105 samples of different crop leaves were collected and analyzed in the laboratory. In each ESU, LAI was derived from canopy measurements made with a LiCor LAI-2000. AHS 80 Airborne Hyperspectral Scanner data were acquired on July 4th 2006. Images were corrected to TOC spectral reflectance with a ground spatial resolution of 6 m (German Aerospace Center 2007) and subsequently resampled to Sentinel-2 spectral bands with spatial resolution of 10 and 20 m. Leaf Area Index was measured by means of the portable canopy analyser Licor LAI-2000. The measurement protocol consisted of three consecutive series of 8 readings covering an elementary surface unit (ESU) of approximately $20 \times 20 \text{ m}^2$.

In total, 45 ESUs (i.e. data points) could be used for the analysis, having LAI between 1 and 4, respectively 19 from SPARC 2003, 16 from SPARC 2004 and 10 from AGRISAR 2006.

The spectral reflectances of the simulated Sentinel-2 images at 10 m and 20 m resolutions, corresponding to each ESU, were extracted from closest pixel to the ESU's centre co-ordinates.

Results

Tables 3, 4 and 5 give the R^2 values, respectively for erectophile, spherical and planophile crop canopies, of linear regressions of VIs, obtained at S2 spectral resolution, versus leaf chlorophyll density (plagiophile and extremophile R^2 values were omitted for brevity). Regressions were obtained for different values of the N leaf structural parameter, different soil types, soil wetness conditions and two sun zenith angles (20° and 40°). In Fig. 2, the R^2 average and standard deviation values ($n = 20$, i.e. 10 soil/soil wetness and 2 sun zenith angles) of VI linear fittings versus leaf chlorophyll density are reported for all classes of leaf orientation and for different values of the N leaf structure parameter.

For most soil/leaf/canopy/illumination conditions considered, the strongest correlations (R^2 values in bold in Tables 3, 4, 5) between VIs and leaf chlorophyll content were obtained by the TCI/OSAVI ratio or by the CVI index. The TCI/OSAVI ratio outperformed all other VI for erectophile canopies (Table 2; Fig. 1 top) and was also the best leaf chlorophyll estimator for all other canopy classes with leaf structural parameters value $N = 1$. On the other hand, the CVI index was the best leaf chlorophyll estimator for plagiophile and extremophile canopies with both $N = 1.5$ and $N = 2$ values and for spherical and planophile canopies with $N = 2$ (Table 4; Fig. 2). For spherical and planophile leaf orientations with $N = 1.5$ (Tables 4, 5; Fig. 2), the TCI/OSAVI ratio and the CVI index overall performances as leaf chlorophyll estimators were comparable, with the former showing the highest average correlation (Fig. 2), and the latter obtaining the highest correlations in more cases (i.e. 12 out of 20 soil/soil wetness/sun zenith combinations both for spherical and planophile canopies, Tables 4, 5).

The $N = 1$ value of the leaf structure parameter is the lowest accepted by the PRO-SPECT model and is not realistic for most crop canopies (e.g. $N = 1.4$ for corn and $N = 1.7$ for soybean, Jacquemoud, et al., 2000).

With the exception of erectophile canopies for which TCI/OSAVI was the best estimator regardless of soil conditions, soil spectral properties appear to determine which index was the best leaf chlorophyll density estimator. The CVI index in general obtained the strongest correlations for darker (i.e. Barnes, H.B.C.—Huston Black Clays in Tables 2,

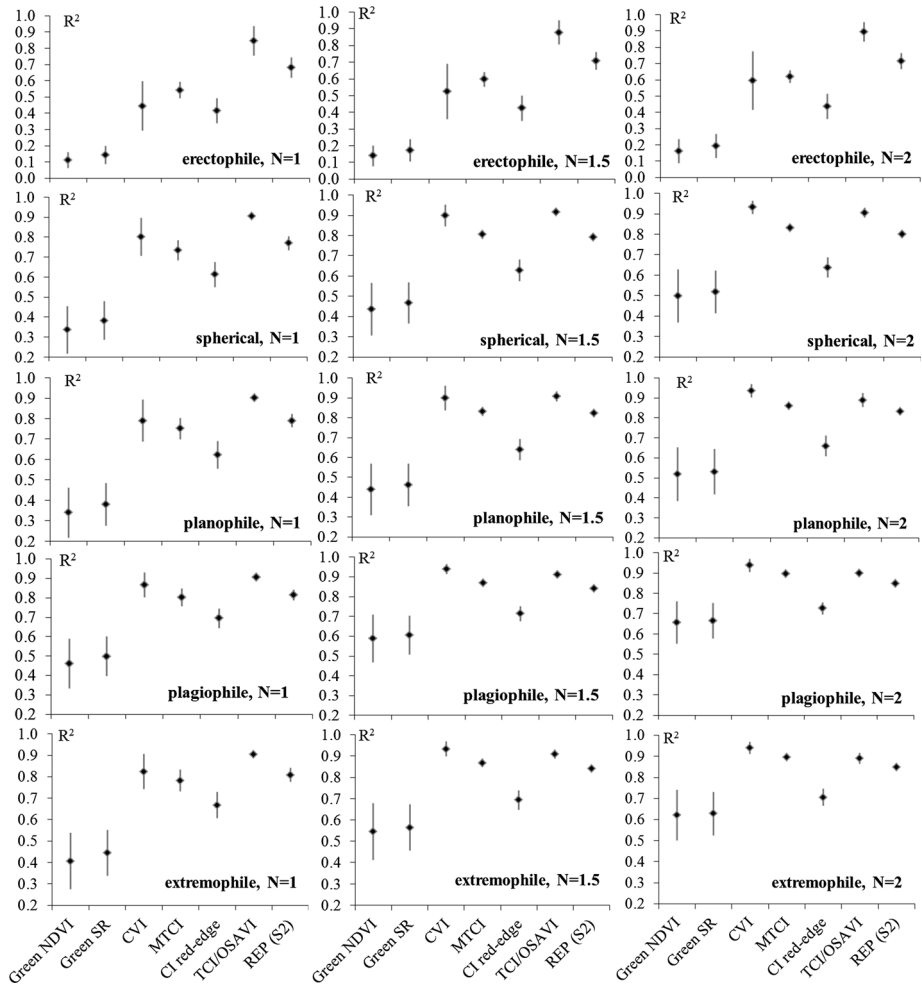


Fig. 2 R^2 average \pm standard deviation ($n = 20$, i.e. 10 soil/soil wetness and 2 sun zenith angles) values of VI linear fittings versus leaf chlorophyll density for different leaf orientation classes and different values of the N leaf structure parameter

3, 4) or wet soils whereas the TCI/OSAVI for brighter (Othello, Cecil, Portneuf, Cordorus in Tables 2, 3, 4) or dry soils. In contrast with the other VIs considered, both the TCI/OSAVI and the CVI indices are LAI-normalized, the former by ratioing with the OSAVI index and the latter by multiplying the Green SR by the red/green reflectance ratio (Table 2).

Besides these two indices, the MTCI obtained the highest correlation only in 6 cases (4 for plagiophile and 2 for extremophile canopies) out of 300 regressions and was in general the third best estimator of leaf chlorophyll (Fig. 2). Hence, results do not confirm previous findings, obtained using older versions of the coupled model, that MTCI can be the best leaf chlorophyll estimator (Vincini and Frazzi 2013) for planophile canopies depending on leaf structure (i.e. crop, genotype). The REP index calculated by linear interpolation from

S2 bands was in general the fourth with the exception of erectophile canopies for which it was the second best chlorophyll estimator, markedly worse, however, than TCI/OSAVI (Fig. 2).

For all canopy classes and all values of the N leaf structure parameter, the $CI_{red-edge}$ was the fifth best chlorophyll estimator and the Green NDVI and Green SR (or CI_{green}), based exclusively on visible and NIR bands like the CVI index, were the worst estimators, with correlation levels constantly and markedly lower than those of the other VIs (Fig. 2).

In Fig. 3, the average RMSE (Root Mean Squared Error, expressed in leaf chlorophyll density units $\mu\text{g cm}^{-2}$) and standard deviation values ($n = 60$, i.e. 10 soil/soil wetness, 3 N leaf structural parameters values and 2 sun zenith angles) obtained by the two best-performing VIs are reported for the different classes of leaf orientation. Taking into account the large variability of LAI values (i.e. the 1–4 LAI range) considered in the synthetic dataset, and its confounding effects on leaf chlorophyll estimation, the RMSE values reported in Fig. 2 are promising for the application of future Sentinel-2 data for variable-rate nitrogen prescriptions. As seen in Fig. 3, besides the superior performances of the TCI/OSAVI ratio for erectophile, the main difference in the performances of the two empirical chlorophyll estimators is the larger variability of the CVI performance depending on the soil background. It is worth noting the performance and portability to different canopy structures, as a leaf chlorophyll density estimator, of the CVI index, not requiring bands in the red-edge, and obtainable at 10 m spatial resolution from Sentinel-2 data. The CVI index obtained high R^2 and low RMSE values for all canopy structures, with the exception of erectophile canopies, and soil conditions (Tables 3, 4; Fig. 2).

The results for the experimental dataset (Table 6) partly confirm what was found in the model-based sensitivity analysis. When data from all crops were pooled together, the CVI index was the best, showing a highly significant correlation with leaf chlorophyll although the R^2 was not very high (0.28 at 10 m resolution) (Fig. 4a). The other indices available at 10 m resolution with S2 also had significant correlations with leaf chlorophyll, in particular Green SR and Green NDVI, although with smaller R^2 values. Of all the indices tested and available for S2 at 20 m resolution, only MTCI had a significant correlation with leaf chlorophyll.

As the sensitivity analysis pointed out, the canopy leaf angular distribution influenced the performance of the leaf chlorophyll indices. For erectophile canopies, including garlic

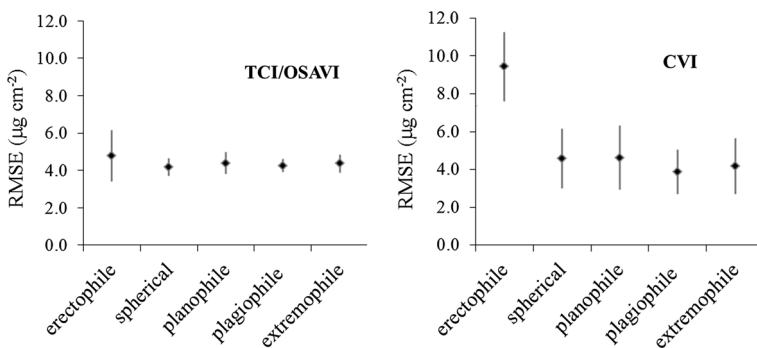


Fig. 3 Average RMSE \pm standard deviation ($n = 60$, i.e. 10 soil/soil wetness, 3 N leaf structure parameter values and 2 sun zenith angles) values of the two best-performing leaf chlorophyll estimators TCI/OSAVI (left) and CVI (right) for different leaf orientation classes

Table 6 Coefficient of determination (R^2) values of VI versus leaf chlorophyll ($a + b$) content for canopies with LAI between 1 and 4 of different leaf angular distribution, obtained from the experimental dataset of ESA SPARC and AGRISAR airborne campaigns, resampling data to Sentinel-2 spectral resolution and spatial resolution of 10 m and 20 m

Index	All canopies					
	Erectophile		Planophile		Spherical	
	10 m	20 m	10 m	20 m	10 m	20 m
NDVI	0.11	<i>0.08</i>	0.02	<i>0.02</i>	0.00	0.27
Green NDVI	0.13	<i>0.08</i>	0.02	<i>0.02</i>	0.03	0.17
Green SR	0.14	<i>0.08</i>	0.05	<i>0.05</i>	0.06	0.28
CVI	0.28	<i>0.18</i>	0.01	<i>0.01</i>	0.19	0.50
MTCI	<i>0.22</i>	0.13	<i>0.07</i>	0.08	<i>0.37</i>	<i>0.67</i>
CI red-edge	<i>0.10</i>	0.05	<i>0.11</i>	0.11	<i>0.02</i>	<i>0.26</i>
TCI/OSAVI	<i>0.02</i>	0.03	<i>0.51</i>	0.62	<i>0.05</i>	<i>0.00</i>
REP _{S2}	<i>0.11</i>	0.04	<i>0.30</i>	0.33	<i>0.29</i>	<i>0.52</i>

Correlations are indicated as statistically significant at * $P < 0.5$, ** $P < 0.01$ or not significant (n.s.). Figures in bold indicate indices compatible with the actual spatial resolution of Sentinel-2 bands, figures in italic those who are not

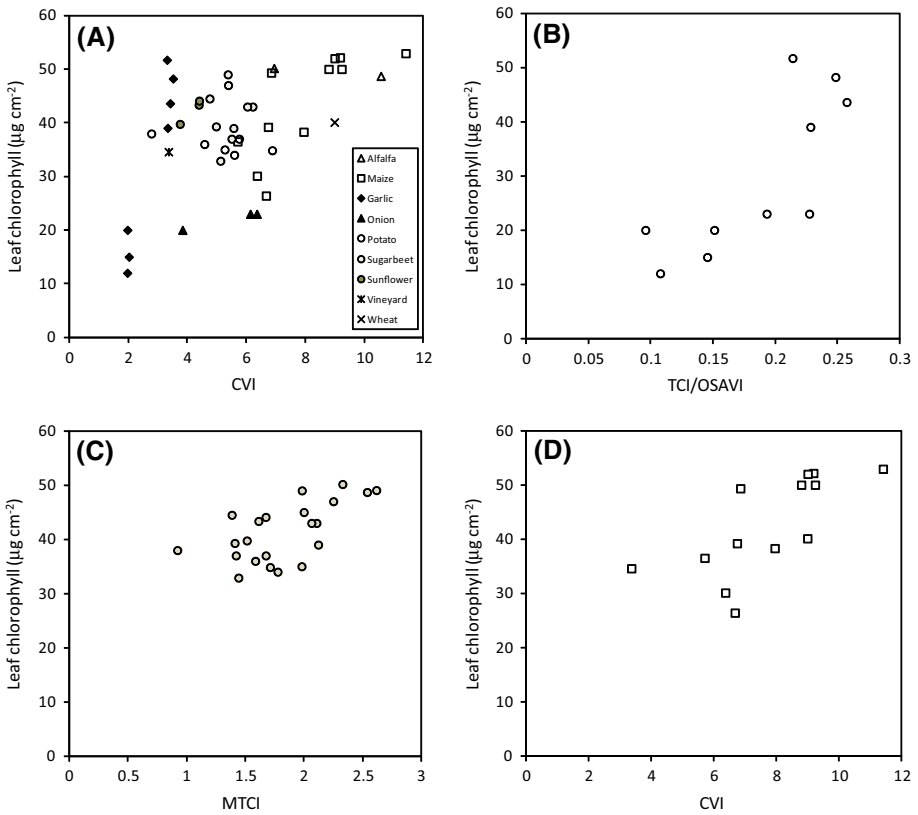


Fig. 4 Relationships between leaf chlorophyll and the best performing vegetation indices for the experimental dataset according to the canopy leaf angle distribution: **a** all crops, **b** erectophile crops (onion and garlic), **c** planophile crops (alfalfa, potato, sugarbeet and sunflower), **d** spherical crops (maize, wheat and vineyard)

and onion, the best results were obtained using TCI/OSAVI (Fig. 4b), with a R^2 even higher at the 20 m resolution (under which this index would be obtainable) than at 10 m. This was in agreement with what was found from the synthetic data analysis. In planophile canopies, including alfalfa, potato, sugarbeet and sunflower, MTCI at 20 m resolution was the best index (Fig. 4c), contradicting results from the model-based analysis and confirming what was found by Vincini and Frazzi (2013). The second best index for planophile canopies was REP, also available with a spatial resolution of 20 m. It should be noted that, for this type of canopy, indices at 20 m resolution (including red edge bands) performed generally better than indices at 10 m resolution (including only red, green and NIR bands). Spherical canopies included maize, wheat and vineyard (only one ESU for each one of these crops). Maize, at an early stage, does not yet have an erectophile leaf angle distribution as found at later growth stages. In this case, the best index at 10 m resolution was CVI (Fig. 4d), whereas, at 20 m resolution, it was MTCI.

Discussion

Canopy reflectance models have been used widely for investigating the response of vegetation indices to the variation of a number of factors and for understanding the mechanisms of interaction among these factors (e.g. Daughtry et al. 2000; Vincini et al. 2008, 2014). The strength of such methodology lies in the possibility of taking into account a far greater range of variability in soil, crop and illumination conditions than could be possibly achieved by using experimental datasets. This gives the opportunity of assessing the robustness of spectral indices in an ideal situation in which there is no uncertainty in the value of the variable to be retrieved (leaf chlorophyll in the present case). In fact, experimental datasets are affected by experimental error, due for example to imperfect sampling. For instance, it is well known that there is considerable variability in leaf chlorophyll content within crop canopies, depending on leaf position (and even within a single leaf) (Ciganda et al. 2012). Due to practical constraints, it is very difficult to carry out a leaf chlorophyll sampling which would correspond perfectly to the penetration depth of a remote sensor into the canopy (Ciganda et al. 2012), for an area corresponding exactly to the remote sensor pixel. Small geometric registration errors typically do occur. Additionally, uncertainty is introduced by the use of leaf meters, even when an accurate calibration is performed (Casa et al. 2015). In the case reported here, actual Sentinel-2 data were not used, so further uncertainty is brought in by the use of resampled data from airborne sensors.

On the other hand, the reliability of results obtained from modelled data depends on the validity of the model. Models are always extreme simplifications of reality, for example, PROSPECT + SAIL assumes no leaf clumping and a homogeneous leaf chlorophyll content throughout the canopy. Therefore the results of model simulation studies should be taken with caution. In this study, the results obtained with an experimental dataset partially confirmed those obtained from the analysis based on model simulations. In particular, they indicated that the CVI index is a potentially interesting index for the estimation of leaf chlorophyll from Sentinel-2 data at 10 m spatial resolution, but that better results could be obtained by differentiating the indices according to the leaf angle distribution. This would require a preliminary knowledge of the crop canopy type which, although not feasible for regional scale applications, could be envisaged in a precision farming context.

It should be noted that in such context, especially for the requirements of the optimisation of nitrogen fertilisation, leaf chlorophyll is a good proxy variable of the crop nitrogen status. In this case, it is quite important to be able to separate nitrogen deficiency from other stress factors. Therefore, the integrated canopy chlorophyll (obtained as the product of LAI and leaf chlorophyll which is more easily obtainable from remote sensing (Baret et al. 2007a)), would be less adequate. In fact, it will be affected by factors acting on LAI, i.e. stand density or water stress, not necessarily linked to nitrogen deficiency.

The simulation results have indicated that leaf chlorophyll content could be theoretically estimated from Sentinel-2 with an accuracy of 4–5 $\mu\text{g cm}^{-2}$, as indicated by the RMSE values of Fig. 3. This would compare well with results obtained from hyperspectral sensors, such as those of Delegido et al. (2010) who reported a RMSE of 4.2 $\mu\text{g cm}^{-2}$ using airborne CASI data. It should be noted that all Sentinel-2 data will be delivered free to the users, providing a considerable advantage over expensive (and not easily obtainable) hyperspectral data, therefore being more suitable for a precision farming context.

Conclusions

Results of a comparison of the sensitivity of best-performing leaf chlorophyll empirical estimators, obtainable from Sentinel-2 spectral bands, and of their portability with the main general classes of leaf inclination and different soil backgrounds, addressed by the analysis of a large PROSPECT5-4SAIL synthetic dataset and of experimental data, indicate that:

- (i) At early phenological stages (i.e. in the 1–4 LAI range), the CVI index, obtainable at 10 m spatial resolution from future Sentinel-2 data, can be used as a leaf chlorophyll estimator at the canopy scale for all classes of leaf inclination, except for erectophile canopies, and soil conditions;
- (ii) However, better accuracy in the estimation of leaf chlorophyll can be obtained by employing different indices according to the prevailing leaf angle distribution of crop canopies. In particular TCI/OSAVI performs better for erectophile canopies and CVI for spherical canopies, whereas MTCI should be preferred for planophile canopies.

These findings can have consequences for the exploitation of Sentinel-2 imagery for variable-rate nitrogen topdressing of different crops. Further work is required to assess the sensitivity of best leaf chlorophyll estimators obtainable at S2 spectral resolution at other viewing angles, besides nadir, for the different main classes of leaf orientation. For such purpose, there is still a need for simulation studies with improved and more realistic models and availability of extensive experimental datasets of good quality.

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