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Crop nitrogen monitoring: Recent progress and principal developments in the context of imaging spectroscopy missions

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Abstract

Nitrogen (N) is considered as one of the most important plant macronutrients and proper management of N therefore is a pre-requisite for modern agriculture. Continuous satellite-based monitoring of this key plant trait would help to understand individual crop N use efficiency and thus would enable site-specific N management. Since hyperspectral imaging sensors could provide detailed measurements of spectral signatures corresponding to the optical activity of chemical constituents, they have a theoretical advantage over multi-spectral sensing for the detection of crop N. The current study aims to provide a state-of-the-art overview of crop N retrieval methods from hyperspectral data in the agricultural sector and in the context of future satellite imaging spectroscopy missions. Over 400 studies were reviewed for this purpose, identifying those estimating mass-based N (N concentration, N%) and area-based N (N content, N_{area}) using hyperspectral remote sensing data. Retrieval methods of the 125 studies selected in this review can be grouped into: (1) parametric regression methods, (2) linear nonparametric regression methods or chemometrics, (3) nonlinear nonparametric regression methods or machine learning regression algorithms, (4) physically-based or radiative transfer models (RTM), (5) use of alternative data sources (sun-induced fluorescence, SIF) and (6) hybrid or combined techniques. Whereas in the last decades methods for estimation of N_{area} and N% from hyperspectral data have been mainly based on simple parametric regression algorithms, such as narrowband vegetation indices, there is an increasing trend of using machine learning, RTM and hybrid techniques. Within plants, N is invested in proteins and chlorophylls stored in the leaf cells, with the proteins being the major nitrogen-containing biochemical constituent. However, in most studies, the relationship between

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N and chlorophyll content was used to estimate crop N, focusing on the visible-near infrared (VNIR) spectral domains, and thus neglecting protein-related N and reallocation of nitrogen to non-photosynthetic compartments. Therefore, we recommend exploiting the estimation of nitrogen via the proxy of proteins using hyperspectral data and in particular the short-wave infrared (SWIR) spectral domain. We further strongly encourage a standardization of nitrogen terminology, distinguishing between N% and N_{area}. Moreover, the exploitation of physically-based approaches is highly recommended combined with machine learning regression algorithms, which represents an interesting perspective for future research in view of new spaceborne imaging spectroscopy sensors.

Keywords

Hyperspectral; Biochemical traits; Radiative transfer modelling; Hybrid techniques; machine learning

1 Introduction

The determination of nitrogen (N) in agriculture has been discussed and studied intensely because N is one of the most important plant macronutrients strongly influencing crop growth, production and quality (Baret et al., 2007; Lemaire et al., 2008). The proper management of N is a pre-requisite for modern agriculture: optimal crop yield from high quality grain can only be obtained with sufficient provision and corresponding uptake of N. Thus, in agricultural practise, N is usually applied via fertilization (Beeckman et al., 2018). Because the actual uptake of N largely depends on the current growth conditions, which are extremely variable in space and time, fertilization is often oversupplied (Skiba and Rees, 2014). Such excessive fertilization causes plant stress and overproduction of leaves, which in turn renders the plants susceptible to diseases (Powell and Lindquist, 1997). Overfertilization also leads to excess N that remains unused in the soil. If this N leaches below the root zone or is lost through run-off, nitrate (NO_3^-) will accumulate in natural water bodies (Jaynes et al., 2001; Padilla et al., 2018). The ecological effects of nutrient overloads are well known as algal blooms or eutrophication of freshwater lakes and coastal areas. This further leads to nitrate contaminated drinking water, which requires expensive treatments. Additionally, nitrous oxide (N_2O) emissions from denitrification and manure decomposition processes on agricultural sites add to the greenhouse gas budget of the atmosphere contributing to global warming (Skiba and Rees, 2014). In summary, both wet deposited forms of N, i.e. ammonium (NH_4^+) and NO_3^-, and gaseous ammonia are harmful to vegetation and therefore have a strong impact on biodiversity through foliar damage, eutrophication, acidification and other stresses. These problems go far beyond agricultural areas: sensitive species are affected within vulnerable habitats often adapted to low nutrient levels, such as grassland, heathland, peatland, forests, arctic and montane ecosystems (Dise et al., 2011).

Nitrogen deficiency, on the other hand, negatively affects photosynthetic assimilation and crop yield both in terms of quantity and quality (Chlingaryan et al., 2018; Jay et al., 2017; Milford et al., 1985). Therefore, fertilizer application rates for optimal economic

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and environmental yield should be considered by taking into account the individual needs of genotypes as well as their actual uptake rates depending on growth stage, soil and weather conditions. Moreover, instead of applying excessive amounts of fertilizer to cover potential crop N demand, the N required according to the target yield should be determined (Lemaire et al., 2008). While monitoring crop N content during the early vegetative growth stages is of major importance for the planning of fertilization measures, assessment of N during mature growth stages provides valuable indication of expected yield quality. Thus, a continuous monitoring of crop N during all growth stages could be of high economic impact (Hank et al., 2019).

With this background in mind, our review study has the following objectives:

- We intend to give an actual overview of crop nitrogen retrieval by means of hyperspectral data and related methods both in view of upcoming spaceborne imaging spectroscopy missions and agricultural monitoring.
- A detailed analysis of the literature will indicate common methods used in the past and identify possible gaps and future trends.
- Finally, the review aims to give recommendations and inspirations for possible new research directions going beyond the traditional methods, and to discuss perspectives of N retrieval from future imaging spectroscopy data streams with associated challenges.

The remainder of the paper is organized as follows. Section 2 introduces the physiology of N and the strong relation to proteins. Section 3 presents the exploitation of reflectance data for the estimation of N or proteins and discusses important N related issues encountered in remote sensing based precision farming. The section also summarizes findings from other review studies. Section 4 discusses the current state of remote sensing retrieval algorithms linked to the estimation of N; Section 5 considers future available satellite missions suitable for N monitoring; Section 6 explains the screening of N studies, classifies applied methods and discusses advantages and limitations of the diverse approaches. Finally, Section 7 summarizes significant research gaps and highlights future perspectives.

2 Nitrogen physiology: constituent of chlorophylls and proteins

The biochemical components of leaves are mainly composed of four elements: hydrogen (H), carbon (C), oxygen (O) and nitrogen (N) with resulting optical properties due to interactions of light with C—O, O—H, C—H, and N—H bonds and stretches (Kokaly and Clark, 1999). N, being taken up by the roots from soil in the form of NH_4^+ and NO_3^-, is a rather small component of leaf dry weight, ranging from 0.3% to 6.4% (Wright et al., 2004). A large amount of N is invested in proteins and chlorophylls within the leaf cells, with the proteins being the major N-containing biochemical constituent of plants (Kokaly et al., 2009). Ribulose-1,5-bisphosphate carboxylase/oxygenase (rubisco) is the most abundant protein in leaves and in the world (Ellis, 1979). It catalyses the carbon fixation at the beginning of the Calvin-Benson cycle (Bassham et al., 1954) and accounts for 15–30% of the total leaf N in C3 species (Evans, 1989; Makino, 2003). Moreover, rubisco is a major source for N remobilization along with other photosynthesis-related proteins

(Masclaux-Daubresse et al., 2010). Chlorophylls are the primary light harvesting molecules in the photosynthesis process converting carbon dioxide and water into carbohydrates (Evans, 1989; Kokaly et al., 2009). The organic molecule of chlorophyll is a porphyrin that contains four N atoms, which act as a stabilizer of the central magnesium ion. However, only very small shares of leaf N (1.7%) are held in chlorophyll pigments (Kokaly et al., 2009). In total, about 19% of leaf N in C3 plants is allocated to light harvesting complexes (Chapin et al., 1987), see also Fig. 1. They are mainly used to synthesise chlorophyll and chlorophyll-binding proteins in both photosystems and thus explain the strong correlation between N and chlorophyll proposed by many studies. The largest part of leaf N (70%) is bound in molecules supporting carbon fixation, which include biosynthetic (~18%) and CO_2-fixing molecules such as rubisco (26%), bioenergetics (5%) and light harvesting (19%), see also Fig. 1 for an exemplarily sun leaf of a C3 plant (Chapin et al., 1987; Kokaly et al., 2009).

Vegetation growth is not a static but a dynamic process of constant nitrogen turnover (Kattge, 2002). For example, early in a growing season N is first bound in vegetative tissues. During the reproductive phase, N is moved or reallocated from the vegetative organs (leaves) to reproductive structures, such as seeds, ears or fruits (Ohyama, 2010). Note that allocation is not an independent process, but the combination of multiple processes involving the assembly and disassembly of N-containing structures, such as proteins, nucleic acids, chlorophyll and phytochemicals, and particularly alkaloids.

Numerous studies have related different kinds of spectroscopic estimation of chlorophyll content to nitrogen, relying on the fact that the two traits are highly correlated. However, the linkage is weak with Pearson correlation coefficient of 0.65 ± 0.15 across ecosystems (Homolová et al., 2013), which can be explained by the minor contribution of N to light harvesting processes, and the different allocations of N, including photosynthesis, storage, respiration and structure (Xu et al., 2012). Some ecosystems, e.g. as the humid tropics, are known for strong decoupling of leaf chlorophyll and N contents (Asner and Martin, 2009). The use of chlorophyll content as proxy for N can be misleading when in reality other mineral deficiencies occur: for instance, the sulphur deficiency symptom leads to chlorosis starting in the emergence of young leaves (Schnug and Haneklaus, 2005). Rust infestation may also be confused with N deficiency, as diseased plants exhibit higher reflectance values in the visible region caused by lower chlorophyll activity (Bravo et al., 2003). Yellowing due to a decrease in chlorophyll of crop leaves may therefore be caused by many factors that are not necessarily related to N deficiency, for instance herbicide injury, liquid fertilizer burn, freeze injury or moisture stress (Kimura et al., 2016). Therefore, decoupling the estimation of chlorophyll and N content from remote sensing data may contribute to improve our capacity to discriminate among various stresses and pathogens. In contrast to chlorophyll, the leaf protein content appears as a strong proxy for leaf N content which may not suffer from the same downsides, as the largest part of leaf N is bound in proteins. Proteins contribute to the different allocations of N (Xu et al., 2012), and strong correlations between N resorption and protein degradation have been evidenced for some species (Yasumura et al., 2007), even if this mechanism is not universally shared among species (Sample and Babst, 2018). The measurement of protein content in food material (including plant tissues) is usually directly derived from the Kjeldahl method which consists in digesting proteins

and measuring the N contained in these proteins, as well as ammonia and ammonium. Traditionally, a nitrogen-to-protein conversion factor of 6.25 was used. Yet, some studies have demonstrated that the factor is invalid for plant materials due to the existence of non-protein nitrogenous compounds (Milton and Dintzis, 1981; Mosse, 1990; Yeoh and Wee, 1994). In this context, different factors have been discussed as reviewed by Mariotti et al. (2008) and a factor of 4.43 was proposed by Yeoh and Wee (1994) for plant tissues after analysis of 90 plant species.

An exemplary relationship between in situ measured canopy chlorophyll content and aboveground nitrogen content (N_{area}) depending on the growth stage of winter wheat and maize is presented in Fig. 2. This finding points toward the limitation of solely using empirical chlorophyll-N relationships to estimate the area-based N content of crop canopies: the correlation between canopy chlorophyll content and aboveground N_{area} decreases as soon as flowers and fruits appear or senescence emerges. This results from the dynamic process of nitrogen turnover, explained before: in the reproductive growth stage, N is reallocated from the vegetative organs to reproductive structures (Ohyama, 2010). Hence, the amount of N in the plant remains the same whereas leaf chlorophyll content decreases.

The relationship among leaf constituents of the Leaf Optical Properties Experiment, LOPEX dataset (Hosgood et al., 1994), confirms these findings: the analysis of the LOPEX data (downloaded from opticleaf.ipgp.fr) revealed a weak correlation (R^2= 0.14) between N and chlorophylls across growth stages and species, which limits the capability of estimating N from chlorophylls. Hereby, in situ observations for > 40 species were collected, including agriculturally relevant crops such as corn, sunflower, rice, potato, alfalfa and cabbage. This illustrates the difficulty to produce robust models for the estimation of plant N based solely on the relation between chlorophyll and nitrogen.

To summarize the physiological discussion of plant-bound nitrogen, we recommend recognizing proteins as the major N-containing biochemical constituent of leaves and plants. The often assumed strong positive relationship between N and chlorophylls is hampered by the fact that only a small part of the total plant N amount is effectively bound in chlorophylls. Moreover, the multiple allocations and remobilization of N leads to a decrease in the relation between chlorophyll content and N under environmental constraints and with beginning senescence at the end of the growing season. Besides, a positive N–chlorophyll relationship is species-specific and thus not applicable for regions with high species diversity (Hallik et al., 2009; Homolová et al., 2013).

3 Hyperspectral sensing and applications in the context of nitrogen

The three processes of absorption, reflection and transmission describe interactions between incident radiation, leaf biochemical constituents and canopy biophysical traits. The reflected solar radiation in the optical domain (i.e. from 380 to 2500 nm) is generally used in studies that analyze vegetation characteristics, since most of the absorption features of green vegetation are located in this part of the spectrum (Homolová et al., 2013; Kokaly et al., 2009). The reflectance in the optical domain can be divided into three spectral parts: the visible (380–700 nm, VIS), which is dominated by absorption of foliar photosynthetic

pigments, such as chlorophylls, carotenoids and anthocyanins; the near infrared (700–1300 nm, NIR), which is dominated by scattering occurring at both leaf and canopy scale and driven, among others, by leaf structure, the leaf area index (LAI) and plant density; the shortwave infrared region (1300–2500 nm, SWIR) which is dominated by absorption of water, lignin, cellulose and proteins. The studies of Thenkabail et al. (2013a) and Hank et al. (2019) provide illustrative figures of the spectral domains and their sensitivity to specific vegetation variables.

For more than three decades, reflectance data from hyperspectral sensors have been used to estimate and monitor biochemical constituents and biophysical traits of vegetation, including foliar N (Hansen and Schjoerring, 2003; Inoue et al., 2012; Peñuelas et al., 1994). The term hyperspectral, used here for simplicity, rather emphasizes a large number of spectral bands without further specification. The more appropriate term would be “imaging spectrometry” or “imaging spectroscopy” according to Schaepman et al. (2006). It can be understood as a passive remote sensing technology simultaneously acquiring spatially co-registered images or signatures in contiguous series of narrow wavebands. The narrow bands are usually provided in spectral sampling distance (SSD) of 10 nm or less. The availability of hyperspectral data does not always imply that the full spectrum was exploited. Instead, one must distinguish between those studies that used data from hyper-spectral sensors for broadband analysis, i.e. resampling of spectral reflectance according to the spectral configuration of different (broad) band sensor systems, e.g. by Prey and Schmidhalter (2019). Hyper-spectral narrowband remote sensing techniques aim at taking advantage of hundreds of bands sensitive to biochemical constituents and biophysical traits (Marshall et al., 2016). There have been numerous studies demonstrating the suitability of broadband methods (and sensors) for the retrieval of structural biophysical vegetation traits, such as LAI (Darvishzadeh et al., 2019; Richter et al., 2012b; Vuolo et al., 2010). However, the usage of broadband methods (and thus sensors) is limited for the estimation of subtle features related to vegetation biochemistry such as proteins due to the fact that only portions of the solar spectrum are exploited and that spectral information is lost at integrating over coarse bandwidths (Ollinger, 2010). For the detection of these fine features, narrowband analysis or chemometric methods (Lavine and Workman, 2013) should be given preference.

In the pioneering work from Curran (1989), distinct absorption peaks of proteins (and nitrogen) were reported, located mainly in the SWIR spectral range (Table 1). These results were confirmed by Fourty et al. (1996), who found a good agreement within a 10 nm - window of protein absorption positions between their own measurements and the bands identified by Curran (1989). Table 1 summarizes specific absorption bands associated with proteins and nitrogen according to Kumar et al. (2001), Curran (1989) and Fourty et al. (1996). The studies reported absorption bands published by previous studies measuring biochemical absorption features (Curran, 1989; Elvidge, 1990; Himmelsbach et al., 1988; Williams and Norris, 1987).

Some of the indicated absorption bands are not only sensitive to proteins or N, but also to other important biochemical components, such as lignin at 1690 nm and 1940 nm, cellulose at 1940 nm and starch at 1690 nm and 1940 nm. In particular, the strong O—H bound at 1940 nm causes absorption of these biochemicals and water simultaneously (Kumar et

al., 2001). This should be taken into account for the estimation of foliar biochemistry from single absorption features.

Biophysical chemical analyses of N are costly, laborious, time consuming and restricted to a limited number of locations and time points, which does not allow for monitoring continuous seasonal development. Instead, this can be accomplished by usage of precision farming techniques. Precision farming is an important component of smart farming, which aims at information-driven optimization of farming systems (Bach et al., 2016) and includes real-time Earth observation contributing to site-specific planning of important management measures such as fertilization (Cidad et al., 2000; Hank et al., 2019). Recently, such satellite-, planes-, drones or vehicle-based remote sensing technologies are becoming important tools in supporting the present management systems. From satellites, multi-spectral imaging systems have been frequently used to obtain information about crop N status (Söderström et al., 2017; Zheng et al., 2018). Mulla (2013) identified the use of hyperspectral remote sensing for variable rate, inseason management of nitrogen fertilizer as “perhaps of greatest interest for precision agriculture”. The implementation of such technologies may also mitigate the negative effects of N on the plant.

Review studies of N retrieval discussing the plethora of multi-spectral systems have been published by Goffart et al. (2008) or Muñoz-Huerta et al. (2013). Both studies highlight the potential of future hyperspectral sensors for N deficiency detection since discrimination of leaf biochemical components can best be achieved by exploiting narrow spectral bands. Moreover, the study of Baret et al. (2007) reviewed the quantification of stress levels from remote sensing observations with N as a key factor. The authors mainly focused on canopy chlorophyll content as a proxy for N based on findings of their previous study (Baret and Fourty, 1997), stating that “there were very few chances to retrieve canopy nitrogen directly or protein content from remote sensing observations, even using hyper-spectral systems” (Baret et al., 2007). This is in accordance with the exhaustive review study of Homolová et al. (2013) who examined optical based plant traits mapping including N. The authors discussed the problem of different scales, such as scaling up from leaf to canopy level and agreement between different kinds of remote sensing observations. Moreover, they presented a comprehensive figure of spectral wavelengths frequently used in scientific literature for estimation of N concentration (N%) and content (N_{area}), showing a broad distribution over the entire optical domain with some pronounced features in the SWIR. As conclusion of their study, Homolová et al. (2013) strongly supported the hypothesis that optical remote sensing of chlorophyll content can be used as an operational proxy for N estimation, based on moderate to good relationships between nitrogen and chlorophyll. In fact, since decades, numerous studies have been published demonstrating a success in N retrieval using chlorophyll as proxy, e.g. Filella et al. (1995). Dale et al. (2013) reviewed various applications of near-infrared hyperspectral imaging (NIR-HSI) in agriculture with plant stresses imposed, among others, by insufficient N fertilization. The authors pointed out that hyperspectral data from macroscopic to satellite level are currently a large opportunity to assess the quality of agro-food products. Weiss et al. (2020) defined N as a secondary agronomic state variable not directly derivable from radiative transfer modelling. Instead, N results from the combination of several processes within the soil-plant-atmosphere continuum and can only be directly derived using empirical approaches. Deterministic

approaches can be used to estimate primary variables (such as chlorophyll content or proteins) by combining land surface process models and remote sensing data. Knyazikhin et al. (2013b) analyzed the link between vegetation canopy bidirectional reflectance factor (BRF) and foliar N% for forests. The authors concluded that three-dimensional (3-D) radiative transfer theory is required to explain the physically consistent linkage between leaf scattering and canopy reflectance, which often neglected by existing approaches. Multiple studies have demonstrated that N% of grasslands or cultivates decreases over the growing season, implying that it negatively relates to dry total biomass (Greenwood et al., 1986; Justes et al., 1994; Tilly and Bareth, 2019). This dropping of crop-specific critical N% during growth can be described by a negative power function, named “dilution curve”. See also Lemaire et al. (2008) for details. In this context, the concept of the nitrogen nutrition index (NNI) has been introduced (Justes et al., 1994; Lemaire et al., 1989), which is the ratio between the actual N% to the optimal (critical) N% value. Hereby, knowledge of plant dry biomass is required. If NNI > 1.0, the crop is provided with sufficient (or excess) N. In contrast, NNI < 1.0 implies N deficiency, leading to crop stress. Considering this dilution phenomenon of N%, Baret et al. (2007) proposed to use N_{area} to calculate NNI instead of N%, since the resulting N excess or N deficiency can be directly quantified (see also Fig. 4 in Baret et al. (2007)).

In summary, it appears that none of these review studies directly examined the potential of protein content as proxy for nitrogen but rather proposed the use of the relation between N and chlorophyll content for nitrogen retrieval. A reason for this may be the lack of satellite imaging spectroscopy missions in the past that could provide time series of narrowband reflectance data covering also the SWIR spectral region, which allows the monitoring of spectral features of proteins. Another explanation may be that the impact of proteins on canopy reflectance is rather small compared to other parameters by contributing with only 2–4% to the total variation of canopy reflectance (Wang et al., 2018). It may therefore be more straightforward to estimate chlorophyll content exhibiting a distinctive signal in the visible spectral domain. Most of the studies highlight the meaningfulness of empirical methods for N retrieval (Clevers and Kooistra, 2012; Homolová et al., 2013), whereas deterministic approaches such as radiative transfer modelling of proteins is still in its infancy. Nevertheless, the physically-based N retrieval would be the only option for a transferable monitoring system within the agricultural context. With our review study we want to stress on these discussions and gaps, and point toward possible new developments.

4 Algorithms for nitrogen retrieval from remote sensing data

Thomas and Oerther (1972) made pioneering efforts to estimate N from remote sensing and were the first exploiting the relationship between foliar N concentration and laboratory-based leaf reflectance measurements of sweet pepper plants. Since then, methodologies for remotely sensed retrieval of N in the agricultural context were further developed and improved. In the years 1991–1992, the NASA Accelerated Canopy Chemistry Program (ACCP, 1994) was established to identify a sound theoretical and empirical basis to estimate N (and lignin) concentrations in vegetation from remotely sensed imagery.

From the controlled conditions of laboratory-based reflectance measurements to field-, airborne and satellite-based studies, a number of effects potentially increase uncertainties of N retrieval. According to Malenovský et al. (2019) three main categories of variability and uncertainty sources can be identified in the context of biochemical and biophysical plant traits retrieval from (satellite) imaging spectroscopy data. The first category includes the errors referred to the sensor, including sensor calibrations, and radiometric, geometrical and atmospheric corrections (Baret and Buis, 2008; Gao et al., 2009). The second category of uncertainties arises from the parameterizations and assumptions specific to retrieval algorithms (Knyazikhin et al., 2013b). The third group involves the acquisition of in situ field data which are the basis for physically quantifying the uncertainty of the derived vegetation traits (Richter et al., 2012a). Our review mainly focuses on the second category and investigates uncertainties, problems and challenges associated with the different methods for the estimation of N.

4.1 Parametric regressions methods

In the last decades, predominantly simple empirical algorithms based on parametric regressions have been used for N estimation from hyperspectral signatures in the agricultural context. These approaches are by far the most applied and largest group of biochemical and biophysical vegetation trait estimation techniques. Parametric regression models include narrowband vegetation indices (VI) exploiting wavelengths mainly in the VIS, red edge, NIR, but also SWIR, e.g. (Chen et al., 2010; Clevers and Kooistra, 2012; Eitel et al., 2008; He et al., 2016; Herrmann et al., 2010; Jay et al., 2017; Moharana and Dutta, 2016; Stroppiana et al., 2009a). Several studies have demonstrated improved retrievals of canopy N when protein-related absorption bands in the NIR and SWIR were incorporated into narrowband indices (Ferwerda et al., 2005; Herrmann et al., 2010; Serrano et al., 2002).

4.2 Linear nonparametric regression methods

Linear nonparametric regression methods, also known as “chemometrics”, were also exploited for the estimation of N. Chemometrics can be summarized as data-driven approaches using mathematical and statistical techniques to extract chemical and physical information from complex data, such as those measured from hyperspectral sensors. In contrast to the statistical linear parametric approaches, chemometrics do not reduce the spectral information to defined indices but rather add value to the data by transforming them into new features (Davies, 2012): principal component analysis (PCA) is a full-spectrum chemometric procedure that converts a set of observations of possibly correlated variables into a set of principal components of linearly uncorrelated variables by applying orthogonal transformation (Liu et al., 2017). In hyperspectral remote sensing, PCA methods are usually applied for spectral dimensionality reduction (Rivera-Caicedo et al., 2017). The principal components can then be used to calculate regression coefficients for the derivation of biophysical or biochemical vegetation traits (=Principal Component Regression, PCR). Stepwise multiple linear regression (SMLR) uses a defined set of wavebands as independent (predictive) variables (Grossman et al., 1996). Within each step another predictive variable is added or subtracted from the set of explanatory variables in the function based on specific criteria, such as the Akaike information criterion (Yamashita et al., 2007). The full-spectrum methods of “partial least squares regression” (PLSR) have been widely used

in chemometrics (Atzberger et al., 2010; Wold et al., 2001). This technique relates two data matrices (i.e. reflectance and corresponding biochemical trait) by a linear multivariate model taking also the structure of these matrices into account. With this characteristic, PLSR goes beyond traditional regression (Wold et al., 2001), transforming the spectral feature space in a way that the resulting factors account for a maximum of variance in the covariance with the target variable(s). PLSR is able to analyze a vast amount of noisy, collinear data, and its precision increases with the increasing number of relevant variables and observations.

4.3 Nonlinear nonparametric regression methods

Further, nonlinear nonparametric regression methods, namely machine learning regression algorithms, have been adopted for vegetation remote sensing (Verrelst et al., 2019). The group of machine learning includes kernel methods such as support vector regression (SVR), e.g. described in Smola and Schölkopf (2004), a kernel-based regularized regression algorithm. One of today's most promising machine learning methods is Gaussian processes regression (GPR), developed by Rasmussen and Williams (2006). These types of machine learning models have excelled in Earth observation problems in recent years and were mainly introduced for model inversion and emulation of complex codes (Camps-Valls et al., 2016). GPR belongs to kernel based methods relying on a solid Bayesian formalism and thus allow for a formal treatment of uncertainty quantification and error propagation (Camps-Valls et al., 2019; Verrelst et al., 2012). As a probabilistic approach, a GPR model is trained to find individual functions to all training data by fitting a mean and a covariance function. Other examples of machine learning include random forest regression (RFR) and artificial neural networks (ANN). These methods have become increasingly popular in image processing for numerous applications, which is due to their reliable performance and robustness (Verrelst et al., 2012). Random forest regression is a data mining method developed by Breiman (2001) combining a large set of decision trees. It is a robust ensemble learning technique able to handle large numbers of input variables. The widely used approach of ANNs makes use of error backpropagation through the network of perceptrons (Waske et al., 2009). A disadvantage of ANNs is that they are prone to overfitting, meaning that they strongly depend on input quality and may struggle with unknown values outside the range in which they were trained (Kimes et al., 2000). Problems of underfitting and - in particular - overfitting are, however, generally applicable to machine learning models. Overfitting occurs when the models learn random fluctuations and noise from the training data in high detail. Performance and generalization capability of the trained models is adversely affected if these features are not present in the validation data sets. Underfitting implies that the model did not capture essential trends in the training process and thus cannot be applied to new data. Alternative machine learning methods could be tested or hyperparameters tuned to improve performance (Verrelst et al., 2019).

4.4 Physically-based methods

As an interesting alternative, physically-based methods using radiative transfer modelling (RTM) offer the advantage of robustness and transferability (Berger et al., 2018a; Kimes et al., 2000), but have not been fully examined for the assessment of crop N (Wang et al., 2015a). Physical modelling of the spectral signal of leaf N content has been discussed controversially. The authors of the original leaf optical properties model PROSPECT

(Jacquemoud and Baret, 1990) – a radiative transfer model based on Allen's generalized "plate model"simulating the optical properties of plant leaves from 400 to 2500 nm based on a limited set of biochemical constituents and a structure parameter – were the first who tested the implementation of protein (as surrogate of N) into the absorption and scattering processes of the model. These and later attempts were abandoned due to the strong covariance of nitrogen with other N-containing compounds rendering the results inconsistent in particular for fresh leaves (Baret and Fourty, 1997; Fourty et al., 1996; Jacquemoud et al., 1996; Kokaly et al., 2009). Wang et al. (2015b) incorporated specific protein as well as cellulose + lignin absorption coefficients into PROSPECT-5 (Feret et al., 2008). In their work, the authors demonstrated the applicability of the leaf optical properties model of separating specific absorption coefficients (SAC) for proteins and successfully evaluated the feasibility of estimating leaf protein content by means of model inversion from fresh leaf spectra in the spectral range of 800–2500 nm. This was possible through recalibration of the SACs using a new calibration algorithm (Feret et al., 2008; Wang et al., 2015b). The approach was applied by Berger et al. (2018b) to an agricultural area using a look-up table (LUT) based inversion of the actual PROSPECT model PROSPECT-D (Féret et al., 2017) adapting the SACs of protein content for fresh leaves from Wang et al. (2018), and coupling it with the actual version of Scattering by Arbitrary Inclined Leaves (SAIL) model "4SAIL" (Verhoef et al., 2007). The SAIL model (Verhoef, 1984) is one of the earliest and to date probably the most popular canopy bidirectional reflectance model (Jacquemoud et al., 2009). SAIL is based on the one dimensional (1-D) model developed by Suits (1972) to simulate the bidirectional reflectance factor of plant canopies which are assumed as turbid medium. Scattering and absorption is simulated by four upward and downward radiative fluxes. The coupling of SAIL and PROSPECT corresponds to the PROSAIL model (Jacquemoud et al., 2009). As recently reviewed by Berger et al. (2018a), PROSAIL has been used for almost 30 years within hundreds of studies in forward and inverse modes for numerous vegetation-related applications. The afore mentioned LUT-based inversion technique consists of computing a cost function - most authors choose the root mean squared error (RMSE) cost function (Danner et al., 2017) - and finding its minimum over a (PROSAIL) data base of simulated spectral signals. The solution is often the mean or median of all spectra within a defined interval, such as 10–20% of the lowest RMSE values. The final solution for the estimated traits corresponds to the mean (or median) of the respective model input parameters (LAI, chlorophyll content, etc.). LUT-based approaches have been applied by numerous studies over the solar domain (Atzberger and Richter, 2012; Danner et al., 2017; Richter and Timmermans, 2009; Wang et al., 2015b; Weiss et al., 2000). Adapted PROSPECT models, e.g. by Wang et al. (2018) and Berger et al. (2018b), provide promising tools to estimate leaf proteins and thus could be further exploited for N retrieval application studies in an agricultural context (actual versions down-loadable from https://artmotoolbox.com/). Scaling up to the canopy level can be performed by implementing a protein-simulating PROSPECT version for instance into the Soil–Canopy–Observation of Photosynthesis and Energy fluxes (SCOPE) model (van der Tol et al., 2009) or coupling it with the Discrete Anisotropic Radiative Transfer (DART) model (Malenovský et al., 2013). The fact that protein absorption features are partly overlaid by absorption of other vegetation properties, such as water content, leads to difficulties by using simple parametric regression approaches for the retrieval (Feret et al., 2018). Thus,

RTMs should be specifically exploited to decouple confounding factors in the estimations of N or proteins, such as water content or canopy structure. The location of the specific protein absorption features (see Table 1) emphasizes the importance of incorporating the SWIR spectral region for RTM-based retrieval applications. Still, the ill-posed inverse problem may occur for which many solutions have been proposed, such as specific merit functions (Wang et al., 2015b) or the object-based retrieval (Atzberger and Richter, 2012). An exhaustive review to this and related topics is given in Verrelst et al. (2015).

4.5 Hybrid methods

Using RTMs, for instance PROSAIL, in combination with machine learning methods leads to hybrid retrieval procedures. Hybrid models offer the advantage of a physical basis provided by RTMs and the computational efficiency and flexible procedure provided by regression methods. While physical models explore the underlying causality between inputs and outputs, machine learning algorithms are able to isolate relevant inputs for a given output from large datasets (Baker et al., 2018). Practically, the machine learning model is trained on a simulated RTM database, thus rendering the need for in situ reference data obsolete during the training stage (Verrelst et al., 2019). The estimation of several biophysical and biochemical variables has been successfully performed with hybrid inversions: for instance leaf area index (LAI) retrieval by combining PROSAIL with ANNs (Verger et al., 2011), and chlorophyll content retrieval combining PROSAIL with RFR models (Doktor et al., 2014).

Table 2 lists the discussed main retrieval methods for N sensing from hyperspectral data within an agricultural context.

5 Satellite imaging spectroscopy missions for N sensing

In the past few decades, remote sensing has become an attractive technique to estimate crop N at the field scale, i.e. agricultural farmland within at least decametric spatial resolutions. In this context, field spectroscopy has been mainly used for biochemical characterization of vegetation during ground based campaigns, for instance by Alchanatis et al. (2005); Clevers and Kooistra (2012); Ecarnot et al. (2013); Li et al. (2010); Thorp et al. (2012). Proximal sensing at field level is locally constrained and often time-consuming. Instead, the monitoring of large areas using imaging spectroscopy has demonstrated advantages for ecological studies in the domains of agriculture, food security, soils, biodiversity, environmental degradation and hazards, hydrology, forestry and others, as reviewed and discussed by Rast and Painter (2019) or Ustin et al. (2004). For agricultural areas, satellites can provide spatially and temporally consistent information over the growing season capturing the biological lifecycle of the crop and spatial heterogeneity of every field on a weekly basis and at low cost (Atzberger, 2013). This is not feasible with field-based spectroscopy, unmanned aerial vehicles (UAV) or airborne sensors, which usually only fly within organized campaigns. For years, there were only two imaging spectrometers in orbit – Hyperion on NASA’s Earth Observing-1 satellite and Compact High Resolution Imaging Spectrometer (CHRIS) on ESA’s Proba-1. Yet, both sensors were not designed for global mapping. Hyperion data were for instance used by Abdel-Rahman et al. (2013) to estimate

sugarcane N concentration by means of a RFR. CHRIS data were exploited by Castaldi et al. (2016) to estimate the grain N uptake of wheat by means of stepwise regression combined with stepwise variance inflation factors (VIFs) analysis and linear mixed effect model (LMEM). Marshall and Thenkabail (2015) compared the estimation of crop biomass as important indicator for N uptake using spectral indices derived from multi-spectral sensor data (IKONOS, GeoEye-1, Landsat ETM+, MODIS, WorldView-2) with narrowband indices from the EO-1 Hyperion sensor. Results demonstrated that hyperspectral narrowband indices could explain 5–31% greater variability of biomass than broadband indices. This finding strengthens the need for satellite data with higher spectral resolution.

The rare usage of satellite imaging spectroscopy will change in the upcoming years with the evolution of several satellite missions that will provide frequent observations of large areas. Thus, a key role for scientists within the field of spectroscopy in optical remote sensing is the challenge of upscaling the developed models from field to spaceborne sensors (Mutanga et al., 2015). An actual overview of hyperspectral spaceborne systems under development, in preparation and recently launched is given by Rast and Painter (2019). Table 3 presents an overview of recently launched and planned spaceborne imaging spectrometer missions, which could be of interest for protein and N retrieval. These missions of interest include for instance the Italian PRISMA (PRecursore IperSpettrale della Missione Applicativa) satellite (Loizzo et al., 2019), launched on 22nd March 2019. Another example is the Hyperspectral Imager Suite (HISUI), developed by Japanese Ministry of Economy, Trade, and Industry (METI), which was launched on 5th December 2019 (Matsunaga et al., 2017). Shortly after, the German Environmental Mapping and Analysis Program (EnMAP) is foreseen for launch in April 2021 (Guanter et al., 2015). It will acquire information over 30-km-wide areas in the across-track direction, with 30 m ground sampling distance, and measure the spectral domain from 400 nm to 2500 nm over 242 spectral bands with a SSD from 6.5 to 10 nm. Examples of other missions are, among others, the Italian-Israeli Spaceborne Hyperspectral Applicative Land and Ocean Mission SHALOM, envisaged for 2022 (Natale et al., 2013). Some missions are still under investigation, as for instance the former Hyperspectral InfraRed Imager (HyspIRI) mission (Lee et al., 2015), now renamed to NASA’s Surface Biology and Geology (SBG), and the high-priority mission candidate Copernicus Hyperspectral Imaging Mission for the Environment (CHIME), described in Nieke and Rast (2018).

The instrumental characteristics of PRISMA, EnMAP, CHIME and similar systems (see Table 3) are very auspicious for N retrieval studies: they cover the SWIR spectral domain where main protein (nitrogen) absorption features are located. The study of Pellissier et al. (2015), for instance, successfully estimated foliar N concentration using a PLSR approach, and concluded that the proposed HyspIRI (SBG) mission is promising for detecting canopy N concentration across multiple forms of managed grasslands. The contiguous sampling of spectral bands by these sensors allows the discrimination of leaf biochemical components such as proteins. It would be optimal if the spatial resolution provided by the future sensors is in accordance with ESA Sentinel-2 sensors (10–20 m) to allow the mapping of small agricultural fields. Nonetheless, a ground sampling distance of 30 m is still acceptable for many agricultural regions and applications (Rast and Painter, 2019). Thus, with all those missions ahead, an era of operational agricultural monitoring systems is about to

start providing for the first time hyper-spectral time series over large areas. This will enable the further exploitation and validation of efficient retrieval algorithms for vegetation biochemical plant constituents such as nitrogen (Hank et al., 2019). Moreover, time series of crop N content are crucial for the management of fertilization timing to be performed at specific growth stages (Weiss et al., 2020). Nevertheless, the availability of these new hyperspectral data streams will also pose a variety of challenges, such as the correction of atmospheric effects (Gao et al., 2009), temporal gap filling (Gao et al., 2008), understanding of floristically mixed pixels (Ollinger, 2010) or uncertainties arising from leaf-to-canopy upscaling approaches (Malenovský et al., 2019). Given the relatively large pixel size of these new and upcoming hyperspectral satellite sensors (with GSD of 10 m to 30 m, see Table 3), the measured signals will always represent a heterogeneous surface composite; meaning that one pixels' signal is the result of the interactions of electromagnetic radiation with several (plant and soil) constituents (Keshava and Mustard, 2002). Therefore, specific techniques, such as Spectral Mixture Analysis (SMA) were explored, as it was done for instance by Lelong et al. (1998) for stress detection and mapping of wheat agronomic variables. A review of available SMA methods and results of endmember variability reduction in SMA is provided by Somers et al. (2011). The handling of large data volumes will also be an issue, but should become feasible in the near future due to the broad availability of artificial intelligence, machine learning and advanced data analytics (Rast and Painter, 2019).

6 Literature review of nitrogen studies for agricultural applications

6.1 Identification and screening of relevant literature

A systematic literature review was carried out including identification, screening, eligibility and inclusion of relevant records, described in the scheme of the Supplementary material (Supplement 1). The ISI Web of knowledge (Gillis, 2018) and ScienceDirect search engines were the main sources for the identification of relevant records. The topics "hyperspectral" or "imaging spectroscopy", and "nitrogen concentration"or "nitrogen content", and "agriculture" were searched in all variations for the period of 1994–2019. After collecting all apparently relevant records (number of studies, n = 426), a first screening process was performed to remove duplicates and references not relevant for the review study, such as conference proceedings or other non-peer reviewed works or reports, resulting in n = 391 papers for further investigation. In the next step, titles and abstracts screening was performed to exclude all studies from other research fields. In the eligibility part, the remaining n = 167 records underwent intensive analysis. We specifically excluded studies with the following criteria:

(1) No direct estimation of N (but chlorophyll content, nicotine, yield, proteins, fiber quality or other proxies);

(2) N of soil was determined;

(3) Forest, shrubs, wetlands or other vegetation types instead of agriculture;

(4) Resampling into multi (super-) spectral data (e.g. Quickbird, Sentinel-2);

(5) Only rough classification of N supply without concrete measurements;

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(6) Review study.

Finally, a total number of 125 records (see Supplement 2) were identified fulfilling the main criterion of crop N estimation with different methods from hyperspectral or imaging spectroscopy data within an agricultural context. From those studies relevant information according to the following criteria were extracted:

- Spectral exploitation: sensor type, sensor with respective spectral domain;
- Retrieval method;
- Usage of terms (N content/concentration or others);
- Geographic location of the experiments;
- Crop types and scale (leaf and/or canopy).

Fig. 3 shows the absolute number of N retrieval studies extracted from our meta-review from 1994 to 2018 that used data from hyper-spectral sensors to estimate N within an agricultural context. This trend also reflects the general trend of remote sensing application studies, as shown for instance by other reviews in the context of agriculture (Berger et al., 2018a; Weiss et al., 2020).

6.2 Sensor systems

Concerning the usage of different sensor systems, it can be observed that predominantly proximal sensing using field spectrometers has been carried out to acquire canopy spectral reflectance in the field (Fig. 4), as it was the case in 75% of all studies. The most used instruments were from the Analytical Spectral Devices (ASD) series, operating in the spectral range from 350 to 2500 nm, used for instance by Stroppiana et al. (2009b); Wang et al. (2013); Yao et al. (2014). Field-based measurements are followed by airborne acquisitions, for instance with Compact Airborne Spectrographs Imager, CASI (Boegh et al., 2002; Chen et al., 2010), AISA Eagle (Nigon et al., 2015) and AVIRIS (Perry and Roberts, 2008). The low use of satellite-based data, mainly from CHRIS/Proba and Hyperion, was already discussed in Section 5. A few studies used laboratory spectroscopy for leaf N simulation (Chen et al., 2019) or additionally simulated reflectance from hyperspectral sensors by means of radiative transfer modelling (Eitel et al., 2008). UAV or drones, offering novel remote sensing tools for precision agriculture, were used for instance by Näsi et al. (2018). All studies cited in this section belong to the list of identified studies (see Supplement 2).

6.3 Retrieval methods

Retrieval methods for crop N used by the identified studies can be grouped into six general approaches, similar to the state-of-the-art retrieval methods categorization of Verrelst et al. (2019), see also Table 2:

- Parametric regression methods, involving the relation of N to narrow spectral bands or derivates, ratio narrowband vegetation indices (NB-VI) and spectral shapes or transformations (Section 6.3.1);
- Linear nonparametric regression methods or chemometrics (Section 6.3.2);

- Nonlinear nonparametric regression methods or machine learning regression algorithms (Section 6.3.3);
- Physically-based or radiative transfer models (RTM) (Section 6.3.4);
- Alternative data sources such as sun-induced fluorescence based methods (SIF) (Section 6.3.5);
- Hybrid or combined techniques (Section 6.3.6).

Fig. 5 gives an overview of the frequency of applied methods within their categories of the n = 125 studies. Note that many of the studies used several approaches; hence the sum of all applied algorithms does not correspond to the total number of studies.

6.3.1 Application of parametric regression methods—The parametric regression models were divided into three main subgroups. Note that further subdivision is possible but exceeds the scope of this study. Fig. 5 indicates nine studies using the correlation of spectral bands or derivatives to estimate N. Tian et al. (2011), for instance, exploited the relationships between the red edge positions (REP) derived from different algorithms and canopy leaf N concentration of field-grown rice. The REP, defined as the position of the sharp change in leaf reflectance between 680 and 750 nm, is mainly related to changes in chlorophyll content (Horler et al., 1983) and thus secondarily to N.

The overall most used approaches with 62% of all identified records were the narrowband ratio vegetation indices. Only few studies pointed out the limitations of the indices-based approaches, such as limited transferability to different sites. For instance, Moharana and Dutta (2016) established regression models for N indices from Hyperion imagery in an agricultural system. The authors found that Simple Ratio (SR) and leaf N concentration indices, exhibiting linear and nonlinear relationships, were completely different from those developed by other studies. Camino et al. (2018) pointed to the importance of SWIR spectral information. They could show that nitrogen indices (NIs) centered at 1510 nm obtained better agreement with N% (R^2 = 0.69) than traditional chlorophyll indices (TCARI/OSAVI R^2 = 0.45) and structural indices (NDVI R^2 = 0.57), which are solely based on the VNIR region. Nevertheless, the major part of the studies in this category estimated plant N on the basis of its correlation to chlorophyll content.

In summary, although these approaches delivered acceptable to good accuracies of N estimation and are fast in calculation and prediction times, it remains questionable whether the full complexity of hyperspectral data observed by a spectroradiometer can be captured by means of transformed data originating from a few discrete spectral bands (Verrelst et al., 2019). The main drawbacks of VI-based retrievals can be summarized in five points according to Atzberger et al. (2011):

(1) The ill-posedness of the inverse problem occurs, meaning that the resulting value of combining two bands can be a result of several different parameter solutions.

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(2) By using only few spectral bands, available hyperspectral information is only partially exploited, and enhanced sensitivity to noise may occur if narrow bands of low signal-to-noise (SNR) were combined.

(3) Sensor-specific calibration may not be transferred to other sensors due to different instrumental characteristics.

(4) Overspecialization or over-fitting can occur, meaning that the established VI-N models are specific to the dataset used for model calibration. This includes sensitivity to crop type, growth stage, underlying soil type, sun-sensor-constellation, time and date.

(5) Finally, the need to collect in situ reference data for model establishment requires man power, availability of instruments for all acquisitions and campaigns organizational efforts.

Some of these drawbacks can be addressed by generating synthetic databases with appropriate RTMs (Hunt et al., 2013), or by the exploitation of hyperspectral reflectance data collected during intensive campaigns in diversified agricultural regions (Thenkabail et al., 2013b).

6.3.2 Use of chemometrics—PLSR proved to be the most popular technique in the group of chemometrics for studying N from hyperspectral data, and follows directly the NB-VI regarding all methods. It was employed by 37% of all studies selected in the review process. This can be explained, among other reasons, by the fact that the classical PLSR method is available in many software packages and is straightforward in implementation. Worth to mention in this context is the highly cited study of Hansen and Schjoerring (2003) who demonstrated that PLSR improved the prediction of N concentration and decreased the root mean square error (RMSE) by 24%, compared to the application of narrowband indices. The authors specifically highlighted that PLSR analysis "...may provide a useful exploratory and predictive tool when applied on hyperspectral reflectance data". The frequent use of PLSR by N studies mirrors its advantage of combining the positive features of PCA and SMLR, as hereby the covariance to the biochemical traits of interest is considered. One should carefully choose the number of components; otherwise overfitting caused by too many components may occur (Hansen and Schjoerring, 2003). Inoue et al. (2012) stated that PLSR may be more suitable than principal component regression (PCR) for predictive purposes since the resulting latent variables (LV) of a PCR account only for variance in the feature space instead of the covariance between the independent and target variables as in case of PLSR. Nevertheless, also the PLSR method may not always provide optimal results due to possible disturbance by certain wavebands (Inoue et al., 2012). Some optimized PLSR methods have been developed to overcome these limitations, such as interval PLSR (Nørgaard et al., 2000).

Stepwise multiple linear regression was applied by Miphokasap et al. (2012) who found higher correlations with N content than by models based on narrowband vegetation indices. The authors illustrated their findings with the utilization of the full spectral domain of the SMLR (400 to 2500 nm). The benefit of SWIR bands was hereby demonstrated by the study of Dunn et al. (2016) who identified the four most important wavelengths for

predicting N uptake by means of a new calibration created by multiple linear regression using 738 nm, 1362 nm, 1835 nm and 1859 nm spectral bands. Since (S)MLR approaches do not compress spectral data to extract most essential information, sensor noise has little chance to be canceled out (Jacquemoud et al., 1995). An advantage of SMLR is that one can focus on spectral regions of interest when the relation to the variable is well-known (Fourty and Baret, 1997). Moreover, SMLR methods may deliver high predictive accuracies but sometimes at the cost of overfitting and large computational loads, in particular when excessive numbers of variables are selected (Yu et al., 2013; Zhou et al., 2018).

All in all, chemometric methods may be able to provide relatively high retrieval accuracies of N estimation. These methods may be also more suitable for N sensing from hyperspectral data as the NB-VI or other linear parametric approaches due to the above discussed advantages of exploiting the full available spectrum. However, with this approach the local calibration and validation limits the transfer of the models to another space and time (Verrelst et al., 2019). A major advantage of the two full spectrum methods PCR and PLSR is that they are able to overcome multicollinearity, which is the inherent problem of (S) MLR (Grossman et al., 1996). Multiple linear regression methods cannot cope with multicollinearity of hyperspectral data and therefore they tend to be unstable which limits their predictive capabilities (Inoue et al., 2018). It also cannot be assured that established components contain the most relevant information of the biochemical property of interest. Regarding computational efficiency, chemometric techniques may be in slight advantage over more complex machine learning regression and in particular compared to RTM-based approaches. Although machine learning models may be more complex to implement than PLSR approaches, they can deliver explicit estimates of uncertainties and can provide higher mapping qualities as found by several studies (Ashourloo et al., 2016; Verrelst et al., 2019). These are important aspects to be considered in view of future operational processing of vegetation properties from spaceborne imaging spectrometer data streams.

6.3.3 Use of machine learning regression algorithms—Regarding the usage of nonlinear nonparametric regression methods, random forest regression, artificial neural network and support vector regression have been applied in almost equal frequency (RFR, n = 10; ANN, n = 8; SVR, n = 9). Pullanagari et al. (2016) compared different nonparametric models (including PLSR, SVR and RFR) regarding their performance to estimate N% of heterogeneous mixed pasture and found that RFR yielded the highest accuracy. Liang et al. (2018) also reported that RFR algorithms largely improved the prediction of N content compared to two VI-models. Artificial neural networks were applied for instance by Yi et al. (2010), who used the advantages of a PCA with an ANN approach and successfully determined N concentration of rice from spectral reflectance. Miphokasap and Wannasiri (2018) estimated N% of sugarcanes: their results indicated higher correlation coefficients using SVR-based Radial Basis Function (RBF) kernel compared to SMLR models. A large comparative study of Yao et al. (2015) evaluated the performance of six different algorithms, including continuum removal, VI, SMLR, PLSR, ANN and SVR to estimate N concentration in winter wheat. Results indicated that all nonparametric methods performed similar with SVR being the most flexible approach regarding the handling of potential confounding factors.

GPR models, in contrast, have only been evaluated in one study of Zhou et al. (2018) who specifically analyzed the influence of spatial resolution on the separation of leaf N signals from the background in rice canopies. Comparing the results of the GPR model with PLSR and VIs, the authors demonstrated that GPR achieved the best prediction of leaf N concentration.

These comparative studies demonstrated that machine learning often yielded higher estimation accuracies than linear nonparametric approaches, mainly for N% predictions (Miphokasap and Wannasiri, 2018; Pullanagari et al., 2016; Yao et al., 2015; Zhou et al., 2018).

Although these studies have demonstrated the feasibility and applicability of machine learning methods for estimating N of different crops, the models have been exclusively trained and calibrated on in situ measured field data as it is the case for chemometrics and parametric regressions. Therefore, it is difficult to physically inter-compare the results using varying spatial resolutions, diverse sensors and model configurations. Regarding prediction time, nonlinear nonparametric regression algorithms can map biochemical and biophysical vegetation traits quasi instantaneously from hyperspectral scenes, in particular when combined with dimensionality reduction such as PCA. Among these machine learning methods, random forests are fastest in training and prediction; they are also less prone to overfitting and can be regarded as robust to outliers and noise (Belgiu and Drăguţ, 2016). The flexibility offered by kernel methods, in particular the GPRs, make them the most interesting candidates to solve nonlinear problems in hyper-spectral remote sensing. These outstanding methods convince with their intrinsic regularization capabilities and low sensitivity to data dimensionality over other methods for vegetation traits retrieval (Tuia et al., 2018). Due to their capability to provide uncertainty intervals of the predictions, GPR methods will certainly play a major role for automatic processing of biochemical vegetation traits mapping in the future, in particular within hybrid retrieval schemes.

6.3.4 Use of radiative transfer models—Only three studies applied a radiative transfer model for N retrieval in an agricultural context: the N-PROSPECT model (Z. Li et al., 2018; Li et al., 2019; Yang et al., 2015). N-PROSPECT is a modified PROSPECT model version, where the SACs corresponding to chlorophylls were replaced with SACs corresponding to N in order to simulate leaf nitrogen density (LND, in $\mu g/cm^2$) at the leaf scale (Yang et al., 2015). In the study of D. Li et al. (2018), crop N status both at leaf and canopy scales could be retrieved through coupling of N-PROSPECT with the SAIL model (N-PROSAIL).

The N-PROSPECT model, however, was restricted to winter wheat since it was calibrated on four winter wheat cultivars. Hence it is only suitable for estimating N content with experimental set ups similar to the calibration situation (Yang et al., 2015). Finally, this model relies on the correlation between leaf chlorophyll content and N, for which limitations have been highlighted in the previous sections.

Researchers from the radiative transfer community are less optimistic that proteins (nitrogen) can be retrieved by means of physically-based methods (Homolová et al., 2013;

Jacquemoud et al., 1996; Knyazikhin et al., 2013a). This is also mirrored by our literature review with only three studies having used RTM-based approaches within the agricultural context to derive N. It is therefore questionable if satellite-based reflectance will allow for an accurate, transferable and physically-based retrieval of N. According to a broad body of research, the accurate estimation of N is mainly possible through indirect correlations with those traits that are more explicitly linked to the radiative transfer - mostly chlorophyll content. Protein content should be the trait of choice according to its strong connection to N. To guarantee transferability and robustness of monitoring systems, these mechanistic approaches are urgently needed. Large training data sets can be established for machine learning models using deductive capabilities of these physical models to extrapolate to predictions not present in collected in situ data in the past (Baker et al., 2018). This shall motivate researchers to further exploit RTMs tailored to simulate the absorption features of proteins for the retrieval of N.

6.3.5 Alternative data sources: SIF—A few studies used sun-induced chlorophyll fluorescence (SIF) as alternative data source to estimate crop N. Jia et al. (2018) assessed the feasibility of quantifying leaf N concentration from SIF based on the response of SIF to chlorophyll content. The authors found that downward SIF yield indices gave more accurate estimation than the upward SIF yield (FY) indices, though measurement with today's available instruments is still difficult. In the study of Camino et al. (2018) a higher accuracy of N retrieval could be achieved when chlorophyll fluorescence was included compared to models only built based on chlorophyll a + b (C_{ab}), dry matter (C_m) or equivalent water thickness (C_w). The contribution of SIF to N estimation may be highly valuable, though only the chlorophyll-based relation to N is taken into account. Ground-based measurement and modelling studies have reported about the suitability of red and far-red SIF for the detection of N deficiency, which affected many parts of the photosynthetic apparatus, including photosynthetic pigments, thylakoid proteins, and the soluble enzymes such as rubisco (Ač et al., 2015; Mohammed et al., 2019). In this review, however, our focus is on the N retrieval studies using reflectance measurements from hyperspectral sensors but not on SIF measurements.

6.3.6 Implementation of hybrid or combined methods—Hybrid techniques denominate a combination of at least two methods in synergic use. In biophysical and biochemical variable retrieval studies, this method is often the combination of machine learning methods and RTMs, thus combining the generalization level of a physically-based method with a flexible and computationally efficient nonlinear nonparametric statistical method (Verrelst et al., 2019). This kind of studies were not found within the identified records which may be explained by the lack of publicity available RTMs involving N (protein) modelling. We thus extend the definition to include studies using different kinds of methods in combination, for instance crop growth and canopy reflectance modelling. As such, Thorp et al. (2012) combined the DSSAT Cropping System Model (CSM) with the PROSAIL radiative transfer model (CSM-PROSAIL). This study also used the relationship between chlorophyll and N content, by applying a conversion factor to calculate the CSM nitrogen state variable (g cm^{-2}) from C_{ab} (μg cm^{-2}).

The additional information of SIF can be exploited in synergy with RTM-based variable retrieval: in Camino et al. (2018) multiple regression models were established to estimate N with and without including airborne retrieved sun-induced fluorescence. The model performance could significantly be increased by combining SIF with PROSAIL derived variables in the regression.

Fig. 6 shows the development of the application of different method-categories over time. In addition to an overall increasing trend, an increasing interest in nonlinear nonparametric regression algorithms and hybrid/combined methods is obvious. There is also a positive trend in the usage of RTMs in view of the slow but steady increase of physically-based modelling of N content (Li et al., 2019; Wang et al., 2015a; Wang et al., 2015b; Yang et al., 2015).

6.4 Use of technical terminology

There is a lack of consistency regarding the terminology within the identified records. Studies estimating nitrogen from remote sensing acquisitions use diverse expressions, for instance N content, N concentration, N uptake, N status, N rate, N accumulation, N density or even only refer to “N” without any unit or additional designation. To enable a valid comparison between nitrogen-related studies, a standardization of terms would be highly desirable. We recommend that the definition and units of nitrogen should be clearly stated in future works.

Moreover, regarding retrieved nitrogen information from remote sensing, we strongly recommend to distinguish between two measures (D. Li et al., 2018; Scott Green et al., 2003; Wang et al., 2015a):

- Area-based measure “nitrogen content” (N_{area}), expressed per surface unit, and e.g. given in [$g \cdot cm^{-2}$] at leaf scale, in [$g \cdot m^2$] at canopy scale, or [$kg \cdot ha^{-1}$] at field scale.
- Mass-based measure “nitrogen concentration” (N%), expressed per leaf mass unit (or other plant organs), usually using dry weight, and e.g. given in [$mg \cdot g^{-1}$] or [%].

The leaf dry mass per unit leaf area (LMA) can be used to convert N % to N_{area} (Baret and Fourty, 1997):

$$N_{\text{area}} = N\% \cdot LMA \quad (1)$$

Hence, plant N content, expressed on a land area basis, is the product of plant N concentration and plant dry biomass in kg ha^{-1} (Chen et al., 2010).

N_{area} is important from a physiological perspective since it is highly correlated to the photosynthetic capacity of leaves and thus to carbon fixation (Evans, 1989; Rosati et al., 2000).

N_{area} is also considered as the candidate trait with the strongest relationship to V_{cmax} and J_{max} (Dechant et al., 2017; Kattge et al., 2009). Expressing the light saturated photosynthetic rate and nitrogen on the basis of leaf dry weight (i.e., N%), this species-independent relationship clusters around a straight line and reaches zero at 0.6 mmol N g^{-1} (Evans, 1989). Osnas et al. (2013) found that leaf traits were primarily proportional to leaf area, but not to leaf mass as suggested by Wright et al. (2004). Moreover, reflectance and transmittance are not directly sensitive to the concentration, but rather to the content of absorbers per unit leaf area. Therefore, N_{area} should be estimated and – if needed – converted into N% using LMA (Baret and Fourty, 1997). The inverse linear relationship of biomass and N% (dilution phenomenon) shows that with increasing growth stage from planting to maturity, crop N concentration decreases while biomass and LAI increase (Chen et al., 2010; Plenet and Lemaire, 1999). Thus, the usage of N content is more useful and suitable to describe optimal N status (Baret et al., 2007). Moreover, as proposed by Kattenborn et al. (2019) for pigments, the area-based measures are more suitable for upscaling purposes from leaf to canopy level. Upscaling leaf N_{area} to aboveground N_{area} only requires an estimate about total foliage (e.g. LAI) and not, as with N%, additional knowledge about dry matter content.

Nevertheless, the identified records of our meta-analysis focused mainly on N%, see also Fig. 7. In contrast, the estimation of the area-based measure, N_{area}, has been rarely performed, as it was also pointed out by D. Li et al. (2018). Unfortunately, confusion about terminology is present, since many studies use the terms content and concentration interchangeably (Fig. 7), as it was also found by Kattenborn et al. (2019) for pigments. One essential reason for the preferred usage of the mass-based measures might be that leaf nutrients are commonly extracted from plant powder without the availability of either the covered area of leaves or ground (Kattenborn et al., 2019). Therefore, field experiments measuring both crop biochemistry as well as structural canopy variables are highly encouraged.

Some studies focused on the estimation of N uptake although this goal might be challenging to be achieved solely by remote sensing. Hereby, the time factor (i.e. crop growth rate) must be taken into account including the N allocation between vegetative and mature or reproductive organs. For instance, in case of paddy rice approximately 80% of total plant N is absorbed from the soil before flowering and stored in vegetative organs. At the same time and subsequently, N is transported from these organs to the ears and the grains (Ohyama, 2010). There is a strong link between cumulative N uptake and aboveground biomass accumulation. A mathematical relationship between these parameters has been introduced by Plenet and Lemaire (1999), including the amount of N present in the shoots as well as the actual aboveground biomass.

Effectively, the aboveground N_{area} could be estimated for a certain point of time by means of remote sensing techniques. The determination of N uptake, instead, is often not straightforward. This could be potentially achieved with the knowledge of N allocation as well as by combining remote sensing with process-based crop growth models.

Finally, it should be pointed out that remote sensing is primarily limited to N retrieval in leaves. It is not possible to directly detect N stored in the soil. The same holds true for plant organs such as tubers, fruits or hardened stalks because radiation in the solar optical domain is not able to penetrate these tissues completely and to transport information about the biochemical content. Accordingly, a reference to “aboveground nitrogen content” seems most appropriate to describe N content at the canopy scale. Nevertheless, we recommend adapting terminology and units according to the related objectives and hypotheses of the specific studies.

6.5 Study locations and analyzed crop types

The largest part of the studies was performed in China (~45% of all studies), which can be easily explained by the large agricultural areas and the increasing usage of remote sensing techniques and other precision farming technology. European countries follow with 27%, with most studies performed in Germany and Italy. The USA with their vast agricultural regions holds 15% of the studies. Studies were carried out in all continents except South America. This large number of countries involved reflects the global interest in optimal N supply for agriculture.

Regarding the crop types, wheat or winter wheat was analyzed with 34% of all studies, followed by rice with 21% and maize with 13%. This mirrors the world’s staple cropping systems with wheat, rice and maize occupying a large part of agricultural areas around the globe (Khoury et al., 2014).

7 Conclusions

In recent years, interest grew in the determination of crop N using imaging spectroscopy (hyperspectral) data (Fig. 3). This need is currently addressed by the launch and planning of several satellite imaging spectrometers - suitable for N sensing due to the included SWIR domain - that will provide scenes over large agricultural areas. High spatial and temporal coverages supplied by these stable instruments optimally designed for the retrieval of nitrogen will allow testing the transferability of all mentioned N retrieval approaches.

From our meta-analysis, we identified some specific problems and limitations: at first, main effort was invested into parametric regression modelling despite the well-known limitations of vegetation indices, mostly not discussed in the studies. The increasing usage of chemometrics with the most popularly applied PLSR method leads to improved retrievals. Nonetheless, chemometrics still suffer from limited transferability and the inevitable need of in situ training data. Among the machine learning algorithms, GPRs were rarely used, although this technique can be considered as one of the most promising regression models providing uncertainties of the estimates. Within all methods, a strong focus on the N-chlorophyll relationship could be identified, neglecting the fact that most N is bound in proteins. Moreover, there is a lot of confusion in used terminology, i.e. N content versus N concentration, or many other terms. We therefore recommend a standardization of terms, using mass-based N (N concentration, N%) and area-based N (N content, N_{area}). In general, a dominance of N%-based studies compared to N_{area}-based studies can be observed, which may be related to the common measurement practices. The apparent estimation of “N

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uptake" from hyperspectral signatures should be handled carefully, because the processes of N allocation between vegetative and reproductive organs and the strong connection to the aboveground biomass accumulation must be considered. However, if there is ground data of biomass available (for instance using LiDAR measurements or biophysical crop modelling) then the term "N uptake" can be appropriate. In all cases, the authors should always provide the appropriate units of their studied measures.

We further recommend the development of leaf RTMs simulating absorption features of proteins. In this way, the retrieval of N solely based on chlorophyll content could be overcome. Nevertheless, one of the main reasons for focusing on chlorophyll measurements and estimations is to understand photosynthetic processes, plant stress and impact to plant growth and development, as well as N uptake. Therefore, decoupling of the estimation of chlorophyll and N content would provide a more pronounced understanding of N allocation within the plant and the origin of diverse stresses. Moreover, the application of hybrid methods, in particular the combination of physically-based retrieval combined with different machine learning algorithms is suggested for N sensing. In this way, a large training dataset can be generated from RTM simulations which reduces the need for collecting in situ training data. Nevertheless, successful validation exercises under various conditions are required to allow for transfer of the proposed hybrid inversion approach to agricultural areas around the globe: therefore, we strongly recommend to organize extensive field campaigns during future hyperspectral satellite sensors overpasses with simultaneous structural (biomass, LAI) and biochemical (chlorophyll, water, nitrogen, LMA) sampling for improved crop N determination from hyperspectral data. Concurrently or independently, proximal sensing studies (using field spectrometers) can help developing the tools and methods to be further applied and validated at the canopy scale using satellite data.

Continuous crop N monitoring may help to understand the transition of N from the soil into the crop, to help farmers to improve their farm management (Hank et al., 2019) and to alert growers about potential shortfalls, thus guiding real-time or long-term fertilizer management plan modifications for future production years. In this way, overfertilization could be reduced preventing harmful effects on the environment, while at the same time a sustainable use of production resources can be maintained. The outcomes of our study propose that a new era of N sensing also beyond agricultural research and applications could be initiated.

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Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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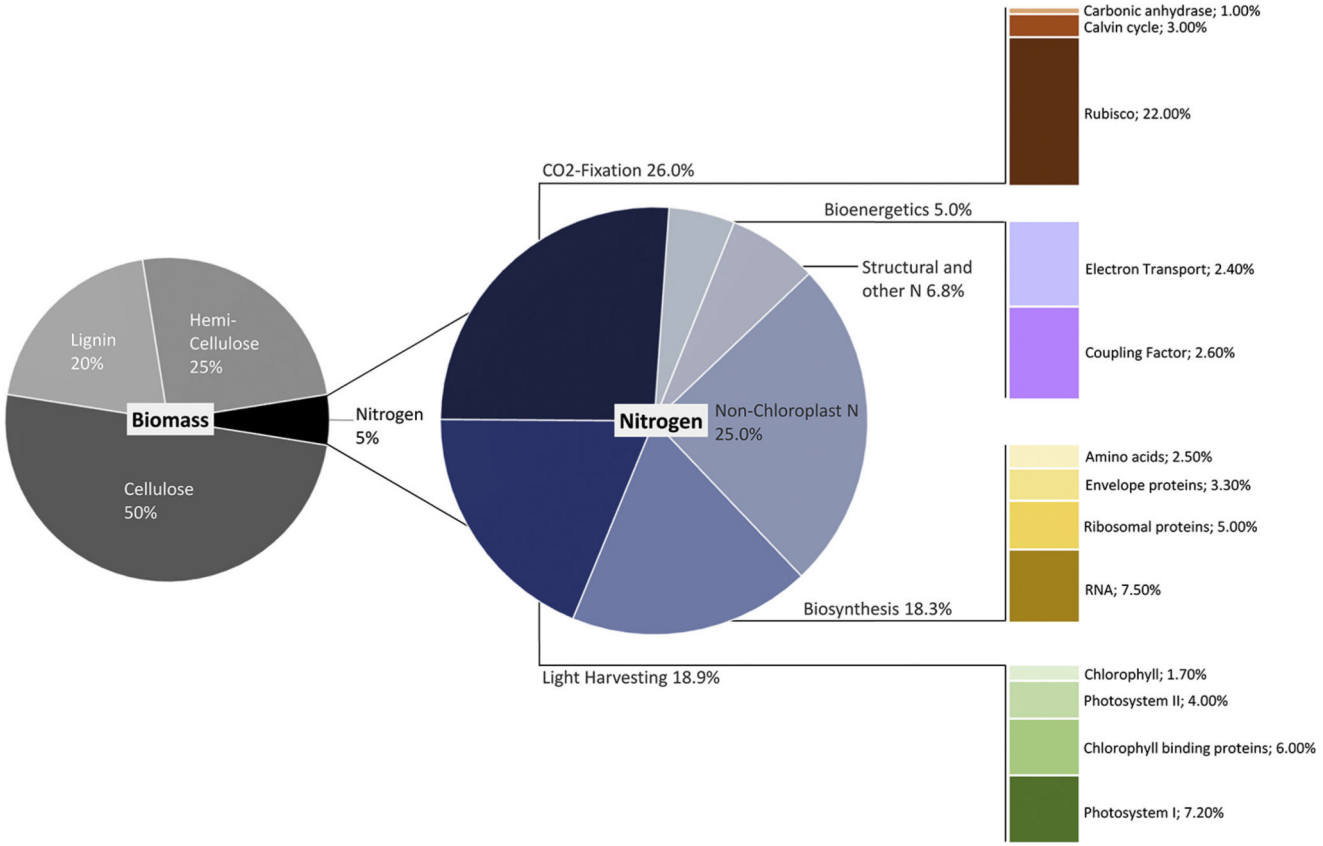

Fig. 1. Nitrogen as key component of biomass (left) and its proportional allocation in a C3 plant leaf (right). Adapted from Chapin et al. (1987).

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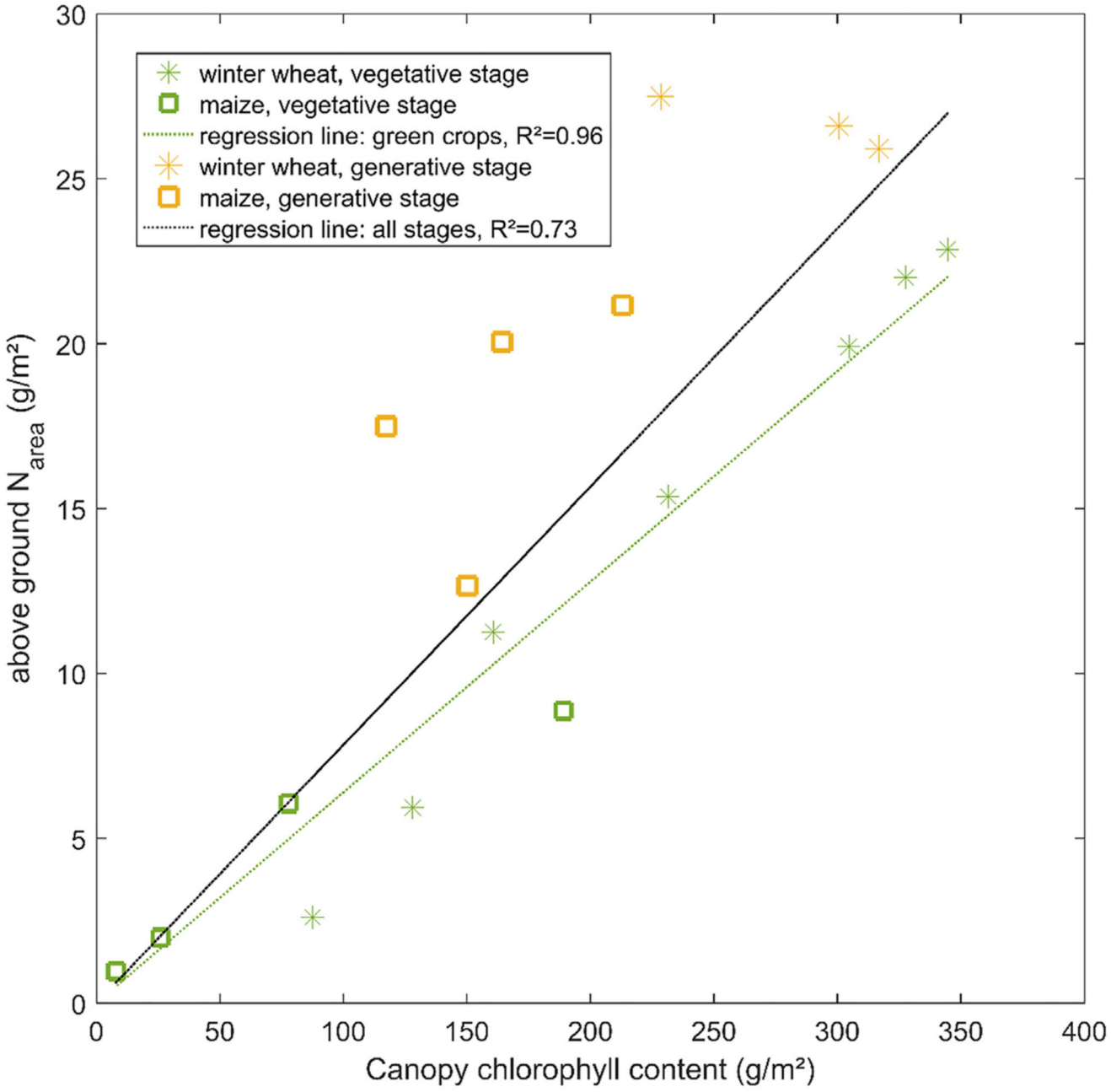

Fig. 2.

Relationship between field measured canopy chlorophyll content (i.e. leaf area index, LAI, multiplied with leaf chlorophyll content, C_{ab}) and measured aboveground N content (N_{area}) as sum of measured N content of leaves, stalks and ears. Regression line in green shows only dates with solely green vegetation (vegetative stage). Regression line in black was achieved using all dates of the MNI field campaign (winter wheat from 29/3–6/7 2017 and maize from 17/7–15/9 2017), as described in Berger et al. (2018b) (Unpublished data). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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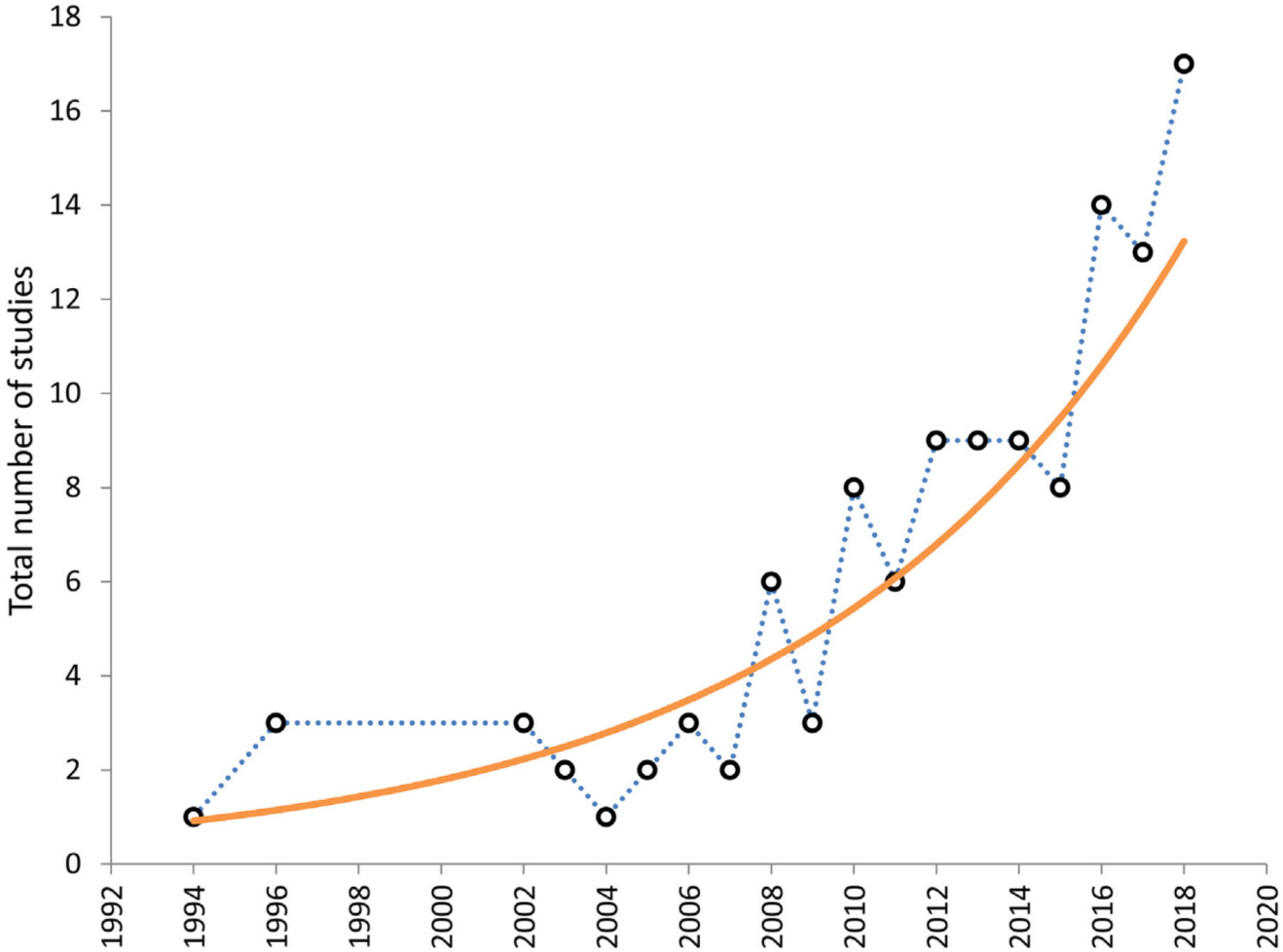

Fig. 3. Absolute number of N retrieval studies per year from 1994 to 2018 as identified by the literature review.

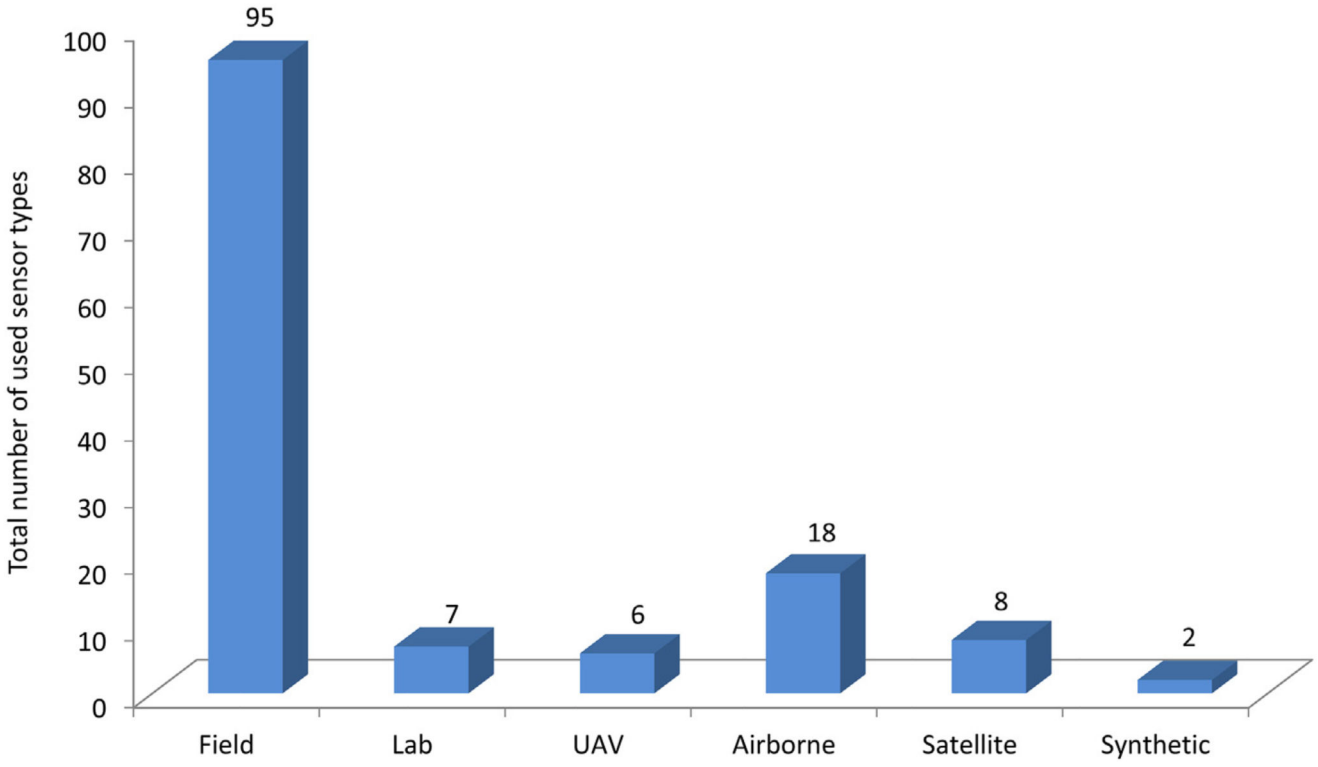

Fig. 4.

Sensor systems used in hyperspectral N retrieval studies. Field: field-based spectrometers, Lab: laboratory analysis (with spectrometers), UAV: sensors on unmanned aerial vehicles, Airborne: sensors on aircrafts, Satellite: satellite-based sensors, Synthetic: simulated reflectance data from hyperspectral sensors, e.g. by RTMs.

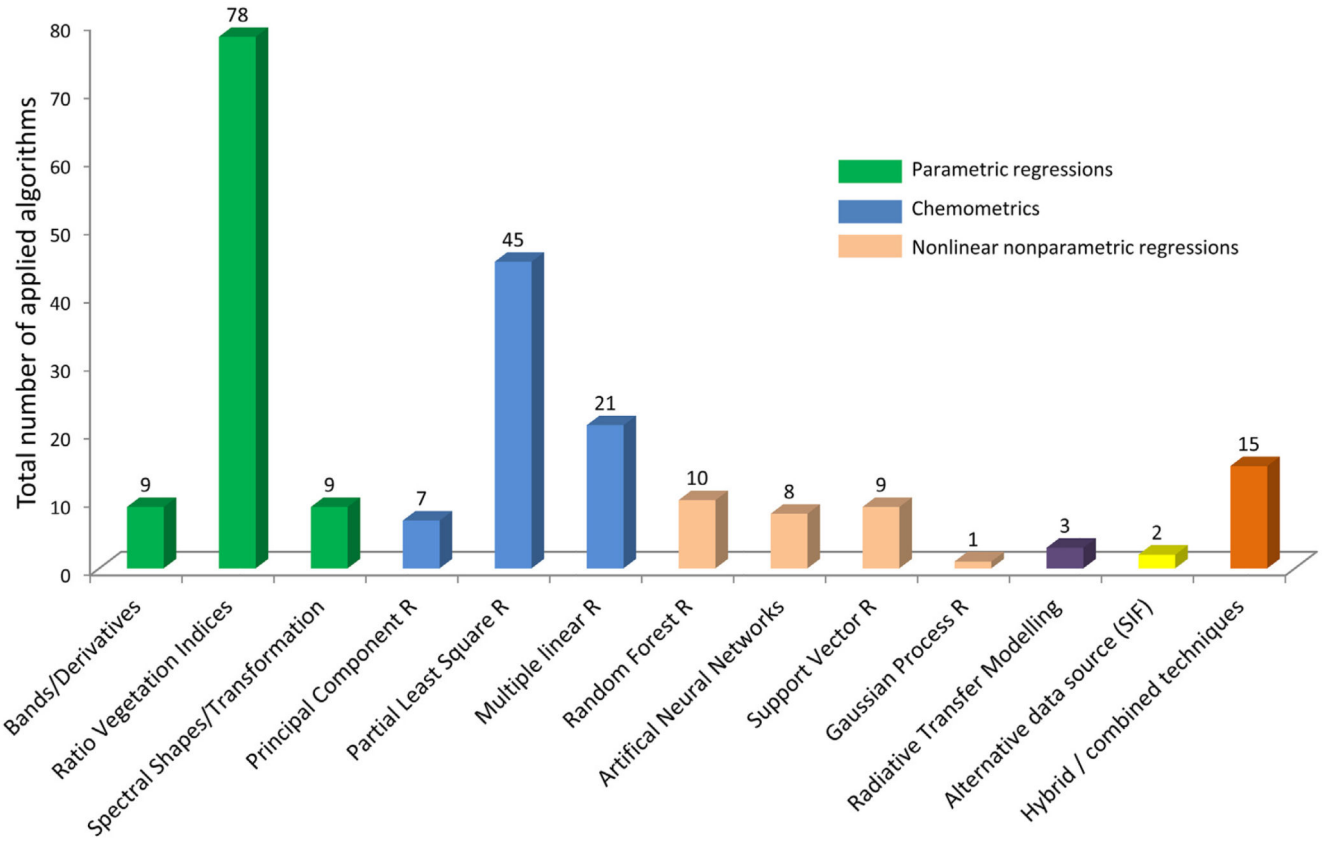

Fig. 5. Identified methods used for the estimation of N content and N concentration.

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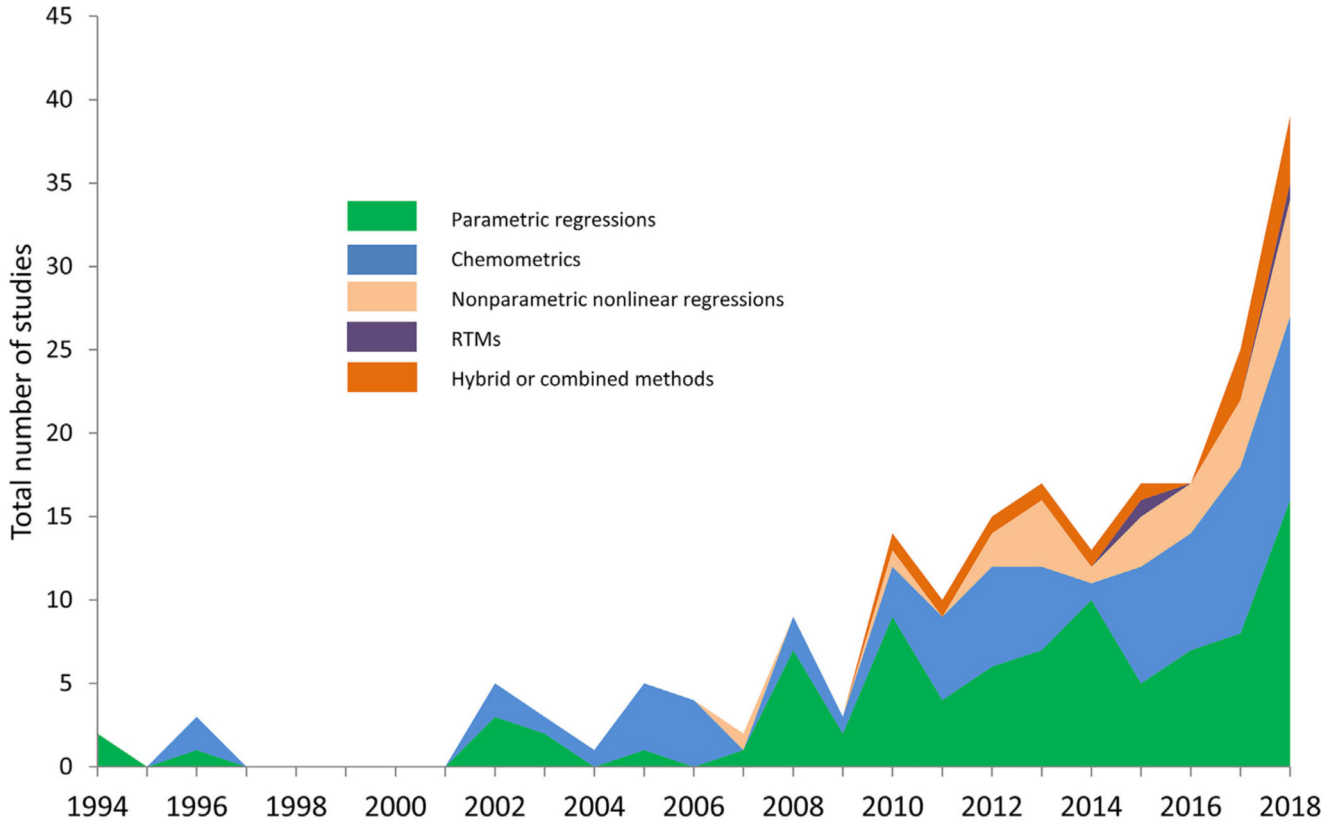

Fig. 6. Development of the five main categories of N retrieval methods in scientific studies over time (from 1994 to 2018).

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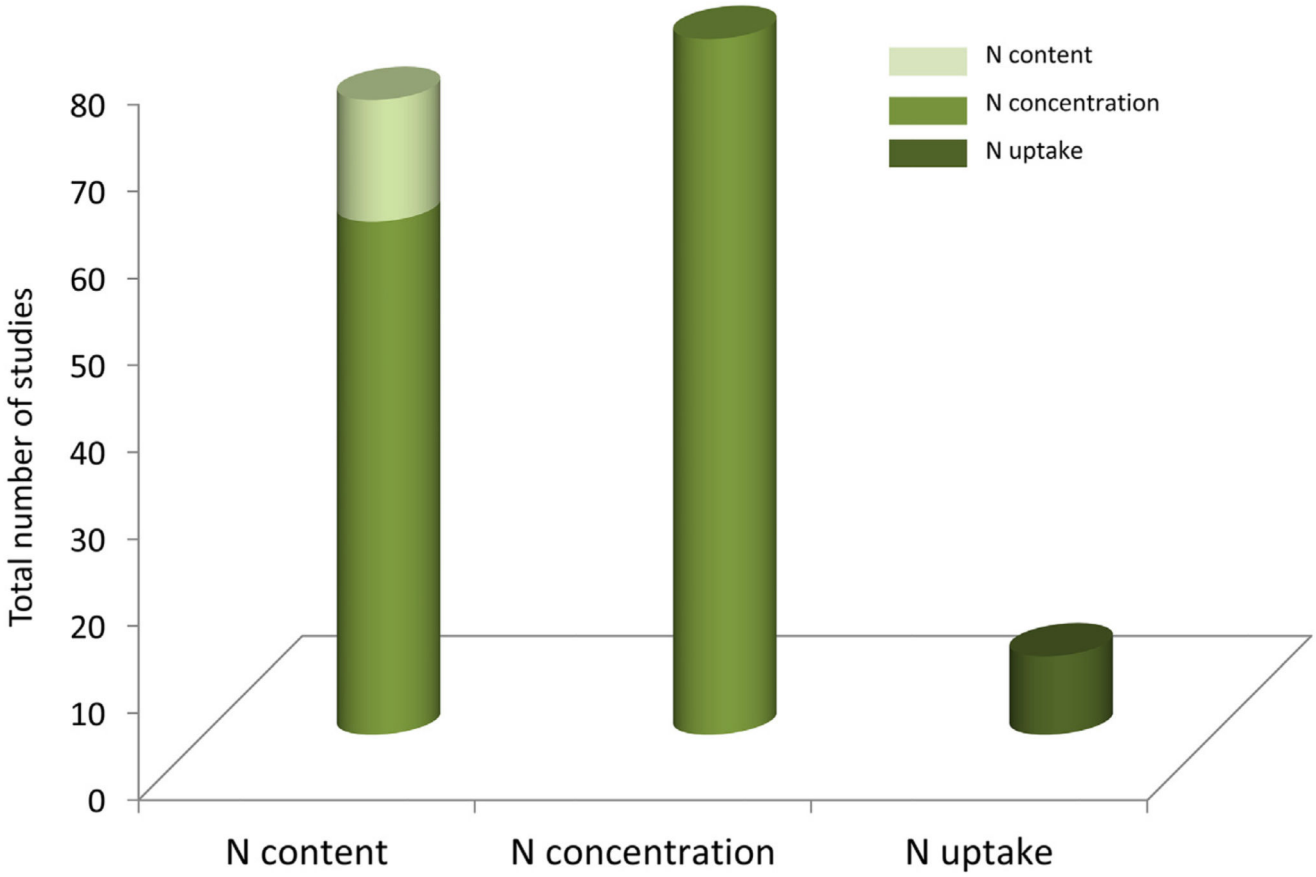

Fig. 7.

Total number of studies apparently retrieving N content, N concentration and N uptake. The color of the bars indicates the in reality estimated measure. For instance, the large part in darker green of the first column (N content) indicates all those studies which in reality estimated N% despite the use of “N content” as terminology. In some cases, more than one term was used in a single study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Table 1

Specific absorption bands associated with proteins and nitrogen and the related absorption mechanisms according to the literature (Curran, 1989; Fourty et al.,1996; Kumar et al., 2001). Wavelength in brackets corresponds to the values remeasured by Fourty et al. (1996).

Wavelength (nm)	Absorption mechanism/electron transition	Absorbing compound
910	C—H stretch, 3rd overtone	Protein
1020	N—H stretch	Protein
1510 (1520)	N—H stretch, 1st overtone	Protein, nitrogen
1690	C—H stretch, 1st overtone	Protein, nitrogen, lignin, starch
1730	C—H stretch	Protein
1940	O—H stretch, O—H deformation	Protein, nitrogen, water, lignin, cellulose, starch
1980 (1960)	N—H asymmetry	Protein
2060	N—H stretch, N=H rotation	Protein, nitrogen
2130	N—H stretch	Protein
2180 (2200)	N—H rotation, C—H stretch, C—O stretch, C=O stretch	Protein, nitrogen
2240 (2270)	C—H stretch	Protein
2300 (2290)	C—H rotation, C=O stretch, N—H stretch	Protein, nitrogen
2350	CH2 rotation, C—H deformation	Protein, nitrogen, cellulose

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Table 2

Overview of main retrieval methods used for N sensing from hyperspectral data in an agricultural context. Categorization according to Verrelst et al. (2019).

Category	Method group, abbreviation	Exemplary references
Linear parametric regressions	Narrowband reflectance or derivative types	(Alchanatis et al., 2005; Goel et al., 2003; Lee et al., 2008)
	Narrowband ratio vegetation indices, NB-VI	(Chen et al., 2010; Herrmann et al., 2010)
	Spectral shapes/transformation	(Feng et al., 2014; Yao et al., 2015)
Linear nonparametric regressions (chemometrics)	(Stepwise) multiple linear regression, (S)MLR	(Castaldi et al., 2016; Miphokasap and Wannasiri, 2018)
	Principal component analysis/regression, PCA/PCR	(Wang et al., 2017)
	Partial least squares regression, PLSR	(Hansen and Schjoerring, 2003; Inoue et al., 2012)
Nonlinear nonparametric regressions (machine learning)	Decision trees (e.g. Random forest regression, RFR)	(Näsi et al., 2018; Pullanagari et al., 2016)
	Artificial neural networks, ANN	(Afandi et al., 2016; Monteiro et al., 2007)
	Kernel-based (Support vector regression, SVR; Gaussian processes regression, GPR)	(L. Li et al., 2018; Wang et al., 2012; Zhou et al., 2018)
Physically-based methods	Radiative transfer modelling, RTM	(Z. Li et al., 2018; Yang et al., 2015)
Hybrid methods	Combination of at least two methods in synergic use	(Song et al., 2011; Thorp et al., 2012)

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Table 3

Overview of recently launched or planned spaceborne imaging spectrometer missions which will potentially provide opportunities for complementary global N sensing. SSD: spectral sampling distance.

Mission (organisation, country)	Spectral range, (SSD, no. of bands)	Spatial resolution (swath)	Launch date	Usage	Reference
PRISMA (ASI, Italy)	400–2500 nm (6–12 nm, 237 bands)	30 m (30 km)	22/03/2019	Technology demonstrator	(Loizzo et al., 2019)
HISUI (METI, Japan),	400–2500 nm (10–12 nm, 185 bands)	20 m (cross-track) × 30 m (along-track) (20 km)	05/12/2019	Operational	(Matsunaga et al., 2017)
EnMAP (DLR, Germany)	400–2500 nm (6.5–10 nm, 242 bands)	30 m (30 km)	04/2021	Scientific precursor	(Guanter et al., 2015)
SHALOM (Italian-Israeli)	400–2500 nm (10 nm, 275 bands)	10 m (30 km)	2022	Operational/ commercial	(Feingersh and Ben Dor, 2015)
CHIME (ESA)	400–2500 nm (210 bands)	20–30 m	tbd	Copernicus high-priority mission candidate	(Nieke and Rast, 2018)
SBG (NASA, U.S.)	350/400–2500 nm (10 nm or better, 210 bands)	30–45 m (150 km)	tbd	Operational	(NASA, 2018)