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NIR and DRIFT-MIR spectrometry of soils for predicting soil and crop . parameters in a flooded field

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Abstract

The increasing popularity of site-specific management (SSM) calls for fast, inexpensive, simultaneous analyses of large numbers of soil variables. The objective of this study was to assess the potential of near infrared (NIR) and diffuse reflectance Fourier transformed in the mid-infrared range (DRIFT-MIR) spectrometry for predicting crop and soil parameters in a flooded California rice field. Two transects of 400 m each were left unfertilized, and 100 sample locations were established. Soil samples were taken in spring, and crop and weed samples at harvest. IR spectra were linked to total soil C and N, mineralizable N, P Olsen, effective cation exchange capacity (eCEC) and exchangeable cations (Ca, Mg, Na and K), as well as yield, N uptake, biomass and weed biomass using partial least squares regression (PLSr). The PLSr models were calibrated using 50 random observations, and validated using the remaining 50 observations. For soil, predictions for eCEC, Ca and Mg were the most accurate, with r^2 values of 0.83, 0.80 and 0.90 for NIR and 0.56, 0.60 and 0.61 for DRIFT-MIR. Correlations for P Olsen were 0.71 and 0.55, and for mineralizable N 0.46 and 0.21, respectively. No significant correlations were found for total soil C or N. For crop parameters, only weed pressure (r^2 of 0.55 and 0.44) and straw biomass (0.30 and 0.34) yielded significant correlations. The correlation with weed pressure was an indirect effect due to better competition by weeds compared to rice under low soil fertility levels. For most parameters, standard errors of prediction were lower than reported in the literature. This indicates that the small range of variability within a field might be the limiting factor in predicting these parameters. It also illustrates the limited use of correlation coefficients in PLSr model validations. We concluded that NIR spectrometry shows promise for SSM, although its predictive power for parameters may vary from site to site. Moreover, predictive models remain unique for specific agroecosystems, and therefore have to be calibrated for every area. The fast and accurate predictions for Ca and Mg concentrations in the soil could be especially important in diagnosing and combating grass tetany, which strongly depends upon Ca and Mg concentrations in the soil.

Introduction

The rising appreciation for the strong controls on yield exercised by short-range spatial variability of natural resources in agricultural fields led to the developing field of site-specific farming or precision agriculture. The variable application of fertilizer, seed varieties, pesticides and other management practices has shown great potential for creating more efficient and sustainable agroecosystems (e.g. Bouma et al., 1999). This shift in focus of agriculture from uniform site management to site-specific management has led to a similar shift in data needs for farmers and researchers. Although accuracy and reproducibility are still essential,

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more attention has been paid to fast, inexpensive, if possible on-the-go analyses of soil and crop parameters. Some of the most popular methods of analysis have been data sources that can be used to predict a variety of soil/crop parameters simultaneously, such as remote-sensing imagery and electromagnetic measurements (e.g. Atherton et al., 1999; Triantafilis et al., 2001).

Infrared (IR) spectrometry in the near- and midinfrared range shows considerable promise for making fast, inexpensive and accurate predictions within a precision agriculture context. Within agriculture, IR spectrometry is already routinely used in predicting protein content, moisture levels and fat content of food products and forage crops (e.g. Wetzel, 1983). More recently, there has been interest in using IR spectrometry for predicting soil properties, especially C and N content and moisture. Morra et al. (1991) predicted organic matter content of clay and silt fractions of 12 different soils using near-infrared (NIR) spectrometry, and reported r^2 values of approximately 0.9 for total organic C and N. Others reported similar results (Ben-Dor and Banin, 1995; Dalal and Henry, 1986; Krishnan et al., 1980). Palmborg and Nordgren (1993) linked NIR spectra to microbiological properties. They reported an r^2 of up to 0.98 for basal respiration and 0.88 for substrate-induced respiration. Milling soil considerably improved r^2 values. More recently, Chang et al. (2001) reported r^2 values of 0.87 and 0.85 for soil total C and N, respectively, over a sample set of approximately 800 soil samples. In addition, they found significant correlations for a number of other soil properties, including mineralizable N, CEC and texture, with r^2 values of 0.72, 0.81 and 0.82, respectively.

The mid-infrared (MIR) spectrum has been often used for qualitative analyses of organic substances. Due to relatively simple sample preparation procedures, diffuse reflectance Fourier transformed (DRIFT-MIR) approaches have been especially popular. Niemeyer et al. (1992) concluded that DRIFT-MIR spectrometry is not suitable for estimating absolute concentrations due to extreme sensitivity of the equipment to homogeneity of the soil/matrix material mixture used in the analysis. However, they were able to estimate relative concentrations of organic matter functional groups. Capriel (1997) defined a hydrophobicity index of soils using the aliphatic C-H reflectance band between 3000–2800 cm⁻¹.

There are a number of studies on DRIFT-MIR spectrometry for characterizing organic matter de-

composition (Cheshire et al., 1993; Spaccini et al., 2001). To our knowledge, there are no studies reported linking DRIFT-MIR spectrometry of soils to crop properties in the subsequent growing season.

None of the above studies were conducted under circumstances deemed typical for precision agriculture (i.e. short-range variability of soil parameters). In addition, none of these studies were done in rice systems, which have unique nutrient cycling properties (especially for N) due to prolonged flooding of the fields. Therefore, the objectives of this study were: (i) to compare the performance of NIR and DRIFT-MIR spectrometry of soils for predicting soil and crop properties in rice systems, and (ii) assessing possibilities for NIR and/or DRIFT-MIR spectrometry under specific precision agriculture conditions.

Materials and methods

Study area

The study area is located at 121°48' W and 39° 30' N in Butte County, on the northeast side of the Sacramento Valley, California. The alluvial soils can be classified as very fine, smectitic, thermic xeric duraquerts and fall within a Lofgren-Blavo series complex (Natural Resources Conservation Service, personal communication). Consistent with the requirements for rice cultivation, the soils are heavy, swell and shrink seasonally, and are poorly drained. The 36 ha field has been cropped with rice (*Oryza Sativa* L.) continuously for over 20 years. Within the field, two transects of 400 m length and 10 m width were established in the spring of 2000. No fertilization was applied on the transects.

Plant and soil samples

On both transects, 50 soil and crop samples were taken for analysis, totaling 100 sampling locations. Forty samples were evenly spaced at 10 m, with 10 additional samples randomly located within both transects. All sampling sites were located using a real-time differentially corrected global positioning system (GPS, model Trimble Pathfinder Pro XRS, Trimble Co.) with an accuracy higher than 0.3 m. Soil samples from the 100 sites were taken on May 3, 2000. Samples were taken from the upper 10 cm. Samples were dried at 65 °C, and milled in a Wiley mill.

Soil samples were analyzed for total C and N, mineralizable N, P Olsen, effective cation exchange

capacity (eCEC) and exchangeable cations (Ca, Mg, Na and K). For total C and N content, a soil subsample was taken, roots were removed by hand using a stereo microscope, and the sample was ball-milled and dried at 105 °C. Subsamples of 30.000 ± 1.000 mg were loaded into silver capsules, the precise weight was recorded, and the capsules were fumigated with HCl to remove any carbonates, following Harris et al. (2001). Total C and total N were determined at the UC Davis Stable Isotope Facility using the elemental analyzer of a continuous flow, isotope ratio mass spectrometer (CF-IRMS, Europa Scientific, Crewe, UK) in the dual-isotope mode, interfaced with a CN sample converter.

Mineralizable N was determined using an anaerobic incubation, following an approach modified from Waring and Bremner (1964) and Bundy and Meisinger (1994). Seven \pm 0.05 g of soil was placed into a flatbottom 50 ml centrifuge tube, and 27.0 ± 0.1 ml water was added. The tube was purged for 15 s with He, closed airtight, and placed in an incubator at 37 °C. After 7 days, 8.0±0.1 ml of 4 M KCl was added, and the tubes were shaken for 1 h on a mechanical shaker. The contents of the tube where filtered through acid-washed Whatman no. 42 filter paper, and NH₄⁺ analyses were done using standard procedures by continuous flow photo-spectrometry. The initial amount of NH4⁺ was determined using the same protocol, without the incubation, and was subtracted from the results. Two replicates for each sample were analyzed.

Extractable P (Olsen) was determined colorimetrically using standard methodology (Kuo, 1996). Exchangeable cations and eCEC, defined as the sum of Ca, Mg, K and Na, was measured at an inductively coupled plasma (ICP) atomic absorption spectrometer after standard extraction with ammonium acetate (Sumner and Miller, 1996). Results for Na were insignificant, and are therefore not reported.

The crop was harvested on September 25, 2000. At all sampling sites, 0.5 m² quadrats were laid out, and all above-ground biomass was hand-harvested with a sickle. Biomass was dried for 72 h at 65 °C, weeds sorted out, threshed, and total biomass, straw biomass, yield, harvest index, and weed biomass was recorded. In addition, total above-ground N uptake and K content were determined.

For N uptake, straw and grain subsamples were ball-milled for 48 h. Subsequently, 9.000 ± 0.500 mg of straw and 3.000 ± 0.500 mg of grain was weighed out in tin capsules, the precise weight was recorded,

and N content was determined similar to soil samples using a stable isotope mass spectrometer.

The K content was determined by an extraction with 2% acetic acid and subsequent analysis on an ICP, following standard procedures.

NIR and DRIFT-MIR spectrometry

Subsamples of the dried, milled soils were ball-milled for 48 h before IR analyses, in order to minimize the effect of aggregate sizes on reflectance spectra (Bowers and Hanks, 1965). For NIR spectrometry, approximately 5 g of ball-milled soil was packed into a natural product cell with a quartz window. The cell was subsequently placed into a Perstorp NIRSystems 6500 spectrometer, and scanned in the visible through NIR range (400–2500 nm), with a resolution of 2 nm. Average spectra for 50 scans were recorded. For all 100 samples, two independent NIR scans were performed on different subsamples.

DRIFT-MIR analyses were subsequently performed on the same subsamples. For this, 1.00 ± 0.05 mg of ball-milled soil was mixed with 30.00 ± 0.50 mg spectrometry grade KBr in a ball mill, overnight. In order to minimize distorting effects of water in the sample, the KBr was stored at 105 °C prior to ball milling. After milling, the soil-KBr mixture was stored at 65 °C in order to avoid degeneration of the soil organic matter under higher temperatures while maintaining dryness. The sample was subsequently analyzed in a Mattson Genesis II FTIRTM MIR spectrometer with a LiTaO₃ detector in the diffuse reflectance mode, in combination with a Pike Technologies EasidiffTM diffuse reflectance accessory. The background scan was done on a pure ball-milled KBr sample. Subsequently, the soil spectra were recorded. Both background and soil sample scans were averaged over 64 scans, with a resolution of 4 cm^{-1} . For every sampling point, two independent soil/KBr mixtures were prepared. Both were analyzed twice, yielding a total of 4 spectra per soil sample. In order to minimize day-to-day fluctuations, a full replicate of 100 samples was done per day.

Data preparation for statistical modeling proceeded similarly for NIR and DRIFT-MIR spectrometry. The following steps were found to give optimal modeling results:

1. Filtering the dataset using a moving average window over the seven closest observations.

	Property	Units	Ν	Min.	Max.	Mean	Median	St. Dev.	CV (%)
Soil	Total C	g kg ⁻¹	100	8.69	16.08	12.77	12.72	1.52	12
	Total N	$g kg^{-1}$	100	0.82	1.30	1.07	1.07	0.11	11
	Mineralizable N	mg kg ⁻¹	99	2.69	11.16	7.57	7.49	1.75	23
	P Olsen	mg kg $^{-1}$	100	5.9	17.7	10.5	9.7	2.9	28
	eCEC	cmol kg ⁻¹	100	21.58	37.99	33.26	33.82	3.20	10
	Exch. K	cmol kg ⁻¹	100	0.36	0.82	0.51	0.51	0.09	17
	Exch. Ca	cmol kg ⁻¹	100	11.70	19.42	17.60	17.83	1.43	8
	Exch. Mg	cmol kg ⁻¹	100	8.29	16.08	13.72	13.92	1.57	12
	Ca/Mg ratio	-	100	1.16	1.44	1.29	1.26	0.07	6
Crop	Grain yield	$Mg ha^{-1}$	89	1.26	4.04	2.55	2.52	0.57	20
	Tot. N uptake	kg ha $^{-1}$	89	19.7	51.6	33.1	32.4	7.0	21
	Total biomass	Mg ha ^{-1}	89	3.90	8.50	5.79	5.70	1.04	18
	Straw biomass	Mg ha ⁻¹	89	2.06	5.48	3.24	3.14	0.71	22
	Harvest index	%	89	28.1	54.2	44.2	45.3	6.1	14
	K content	%	100	1.23	2.46	1.63	1.60	0.20	12
	Weed pressure	Mg ha ⁻¹	100	0.13	1.61	0.67	0.62	0.31	46

Table 1. Descriptive statistics for soil and crop parameters

*Biomass and N uptake refer only to above-ground measurements.

- 2. Baseline correction by subtracting all reflectance numbers with the minimum reflectance of the spectrum.
- 3. Normalizing the spectrum by dividing all reflectance data by the average reflectance of the spectrum.
- 4. Calculating the average normalized spectrum over the different replicates (i.e. two for NIR, four for DRIFT-MIR).
- 5. Thinning out the dataset because of computational constraints, resulting in a 10 nm resolution for the NIR, and a 16 cm⁻¹ resolution for the DRIFT-MIR.

Data analysis

The spectra were modeled using Partial Least Squares regression (PLSr; Esbensen, 2000; Martens and Naes, 1989) using the UnscramblerTM version 7.61 (Camo A/S, Trondheim, Norway) software package for multivariate modeling. PLS regression reduces large numbers of correlated data (in our case IR reflectance spectra) into a limited number of orthogonal components, which are used in a multivariate regression on the independent variables (in our case the selected soil and crop variables). Compared to principal component regression (PCR), PLSr only selects components that are relevant to the requested model; i.e. strong components that are not correlated to the soil

and crop variable in question are not included in the final model. Compared to PCR, this results in simpler models with similar or better predictive capabilities. For more details, see Martens and Naes (1989).

The PLSr model was built using a calibration set of 50 randomly selected observations. Subsequently, the model was validated using the remaining, independent 50 observations. Both the r^2 and the root mean standard error of the prediction (RMSEP) were recorded. The number of components, as well as the parts of the spectra to be included were interactively optimized in order to minimize the RMSEP.

Results

Soil and crop data

Average soil properties are consistent with heavy rice soils: high eCEC values and basic cations (especially Mg), relatively low organic C and N, high P Olsen (Table 1). Total organic C varied from 8.7 to 16.1 g kg⁻¹, and mineralizable N from 2.7 to 11.2 mg kg⁻¹. Variability within the field was highest for P Olsen, with a coefficient of variation of 28%, and values ranging from 5.9 to 17.7.

Portions of the transect close to the borders of the field were accidentally fertilized. These locations were removed from the crop data set, resulting in a total

Table 2. Statistics on the predictive ability of NIR and DRIFT-MIR spectrometry for soil and crop parameters using an independent validation set (n = 50). RMSEP = Root Mean of the Squared Error of the Predictions, RPD = Ratio between RMSEP and standard deviation.

	Property	NIR				DRIFT-MIR			
			RMSEP	RDP	Cat. ^a	r^2	RMSEP	RDP	Cat. ^a
Soil	Total C	0.01	1.59	0.95	С	0.01	0.155	0.98	С
	Total N	0.20	0.10	0.57	С	0.02	0.011	1.03	С
	Mineralizable N	0.46***	0.03	1.47	В	0.21*	0.04	1.06	С
	P Olsen	0.71***	1.6	1.81	В	0.55**	1.9	1.49	В
	eCEC	0.83***	1.36	2.36	А	0.56**	2.08	1.54	В
	Exch. K	0.11	0.07	1.10	С	0.36***	0.08	1.09	С
	Exch. Ca	0.80***	0.66	2.17	А	0.60***	0.93	1.54	В
	Exch. Mg	0.82***	0.69	2.27	А	0.61***	1.04	1.51	В
	Ca/Mg ratio	0.65***	0.05	1.59	В	0.63***	0.04	1.63	В
Crop	Yield	0.04	0.58	0.98	С	0.08	0.55	1.03	С
	Tot. N uptake	0.19	6.4	1.06	С	0.05	6.1	1.11	С
	Total biomass	0.00	1.03	0.98	С	0.14	0.93	1.09	С
	Straw biomass	0.30**	0.52	1.20	С	0.34***	0.50	1.23	С
	Harvest index	0.32**	5.1	1.20	С	0.14	5.69	1.08	С
	K content	0.16	0.16	1.25	С	0.02	0.20	1.00	С
	Weed pressure	0.55***	20.89	1.48	В	0.44***	25.88	1.19	С

*, **, ***: Significant at the 0.05, 0.01 and 0.001 level, respectively.

^a: categories of the prediction power of the PLS model. A: RDP > 2.0; B: RDP = 1.4–2.0; C: RDP < 1.4, following Chang et al. (2001).



Figure 1. Median, maximum and minimum values of the smoothed, baseline-corrected and normalized NIR spectra of the soil.



Figure 2. Fig. 2. Median, maximum and minimum values of the smoothed, baseline-corrected and normalized DRIFT-MIR spectra of the soil.

of 89 observations for biomass, yield and N uptake data (Table 1). For the crop parameters, yield varied considerably over the field, with a range from 1.3 to 4.0 Mg ha⁻¹. Total N uptake, total biomass and straw biomass showed a corresponding range of variability. Weed biomass, mainly rice field bolrush (*Scirpus mucronatus*), ranged from 0.1 to 1.6 Mg ha⁻¹.

Reflectance spectra

The soil spectra can be characterized by high reflectance in the visible range (approximately 400–800 nm) and three major peaks in the near infrared range (approximately 1000–2500 nm). These spectra are largely similar to those reported in other studies (Börjesson et al., 1999; Chang et al., 2001), and only differ in rel-



Figure 3. Ranked correlation coefficients (r^2) for predictions using PLSr for NIR and DRIFT-MIR spectroscopy.

ative height of the respective peaks. The peak at 1900 nm can be largely attributed to remaining moisture in the samples, although this peak is also influenced by organic phosphorus. The peak around 1400 nm can be largely attributed to hydroxyl groups (Palmborg and Nordgren, 1993).

Figure 2 shows the same parameters for the corrected, filtered and normalized DRIFT-MIR spectra. The high peak around 1200–900 cm⁻¹ denotes stretching of Si-O-Si bonds and Al-O-Si within clay minerals, and peaks between 900 and 500 cm⁻¹ reflect other clay mineral characteristics (Haberhauer and Gerzabek, 1999; Haberhauer et al., 1998; Orlov, 1986). Peaks between 3600 and 3300 cm^{-1} and around 1600 cm^{-1} are strongly influenced by stretching and bending of O-H bonds in water, respectively (Johnston and Aochi, 1996). The smaller peaks round 2900 are associated with aliphatic C-H stretching. O-H, N-H and C-H stretching results in various peaks in the $3500-3000 \text{ cm}^{-1}$ region (Baes and Bloom, 1989), whereas stretching and bending of various C–O, COO and CH_x bonds will influence the 1650–950 cm⁻¹ area (Stevenson, 1994). The peak around 1600 cm^{-1} can be due to C=C bonds in aromatic rings, as well as aromatic C-H bonds. However, these peaks may be obscured by bands from H₂O and minerals.

Predicting soil and crop properties by PLSr

The coefficients of correlation between actual measurements and predictions by PLSr using the independent validation set of 50 samples are listed in Table 2. In addition, the RMSEP and the ratio of standard deviation to RMSEP (RDP) are listed. The RDP values are classified according to three categories of performance, following Chang et al. (2001). Figure 3 ranks the correlation coefficients for the NIR spectra. For NIR spectrometry, eCEC and exchangeable Ca and Mg correlated best with the PLSr predictions with highly significant r^2 values above 0.8. RDP values of these properties were all in the highest RDP class (Table 2). Figure 4 plots the predicted values for eCEC and P Olsen against the actual measurements. Among the soil properties, mineralizable N, P Olsen and Ca/Mg ratio have highly significant correlation coefficients, but only a moderate predictive power (RDP classification). Total C and N, as well as exchangeable K, are not significant according to both r^2 values and RDP classification.

PLSr of the NIR spectra yielded significant correlation coefficients for straw biomass, harvest index and weed pressure. However, only the predictive power of the weed pressure model, as expressed in an RDP of 1.5, fell within the highest classification

Figure 5 shows the combined correlation coefficients for the spectra for all soil and crop properties with an RDP higher than 1.4 (Martens and Naes, 1989). Most properties have their own unique correlation pattern, although there seems to be a strong similarity between mineralizable N and weed biomass. Similarly, the patterns for Ca and P Olsen look similar from 500 to 2300 nm. The water peak around 1900 nm was removed from the model or insignificant for all properties except weed biomass and Mg content.

DRIFT-MIR spectrometry did not produce any PLSr models with an RDP higher than 2.0. The best results were obtained for Ca, Mg and their ratio, with r^2 values above 0.6 and RDP's above 1.5. P Olsen and eCEC have r^2 values around 0.55. PLSr models for exchangeable K, total C and N and mineralizable N all have RDP's around 1, indicating no or insignificant predictive power. The combined correlation coefficients for the DRIFT-MIR spectrometry are shown in Figure 6. The area between 4000 and 3500 cm⁻¹ was largely excluded from the PLSr models.

Discussion

Performance of NIR and DRIFT-MIR spectrometry

The predictive power of NIR and DRIFT-MIR spectrometry combined with PLSr varied considerably for the different soil and crop properties, and is sometimes inconsistent with results reported in the literature (Table 2; Figure 3). In particular, the non-significant r^2 values for predicting total soil C and N seem disap-



Figure 4. Validation of the PLS predictions from the NIR spectra for (a) eCEC and (b) P Olsen, using an independent test set (n = 50).



Figure 5. Regression coefficients for the NIR spectrum in the PLS models, for soil and crop parameters with a significant correlation with the spectra.

pointing. However, these results should be qualified. Table 3 lists the r^2 values for predicting organic C or organic matter for a number of studies from the literature. Four out of the five studies reported an r^2 close to 0.9 or higher, with Krishnan et al. (1980) reporting an r^2 of 0.98 for soil organic C. All these studies reported a considerably higher variability in soil properties than our dataset. For example, the ranges of organic C over all analyzed samples were approximately 21, 90 and 284 g kg⁻¹, compared to 7 g kg⁻¹ in our study (Table 3). It is also noteworthy that Krishnan et al. (1980), who reported the smallest number of observations, used a nonlinear regression model, and did not perform a validation test, reported the highest



Figure 6. Regression coefficients for the DRIFT-MIR spectrum in the PLS models, for soil parameters with a significant correlation with the spectra.

Table 3. Results from previous studies on using NIR spectra for predicting soil organic matter or organic C content.

Study	N	Range	r ^{,2}	SEP	Model ^a	Validation				
Organic C, g kg ⁻¹										
Chang et al. (2001)	802	1.3-285.8	0.87	7.9	PCR	independent validation				
Dalal and Henry. (1986)	24	4.2-25.1	0.93	1.6	MLR	cross-validation				
Morra et al. (1991)	12	0.5-90.2	0.93	5.9	MLR	cross-validation				
This study	100	8.7–16.1	0.01	1.6	PLSr	independent validation				
Organic matter, %										
Ben-dor and Banin. (1995)	91	0.1-11.6	0.55	1.3	MNR	independent validation				
Krishnan et al. (1980)	10	1.1-5.1	0.98	-	MLR	no (cross)validation				

^a: PCR = principal components regression; MLR = multiple linear regression; PLS = partial least square regression; MNR

= multiple nonlinear regression.

correlation. The three studies with the highest number of observations and independent validation report the lowest correlation. This suggests that over-fitting might have occurred in some of the studies with low numbers of observations.

In this respect, our SEP of 1.6 g kg⁻¹ is the lowest of all values listed in Table 3. This indicates that the predictive power of our NIR analyses for organic C may be as strong as in the other studies, but that variability of organic C within our field was too low to yield significant results for correlative purposes.

Predicting variability of N uptake by the crop within a field has been notoriously difficult. In a recent study, Walley et al. (2002) compared the performance of five different sophisticated N availability indices in predicting N uptake across a wheat field. None of the indices explained more than 23% of the variability, with total soil C in the top layer performing with similar or higher accuracy. It is therefore remarkable that Börjesson et al. (1999) reported promising results in using NIR spectrometry for predicting N uptake of winter wheat in 15 different soils. Using cross-validation, they reported a correlation coefficient (r^2) of 0.81, compared to 0.60, 0.76 and 0.58 for incubations, mineral N and soil organic matter content, respectively. Compared to those results, our r^2 value of 0.19 seems particularly low. However, the N uptake in that study varied from 29 to 131 kg N ha⁻¹, partly due to the extreme variability in soil resources in the study area. In contrast, our N uptake varied from 20 to 52 kg N ha⁻¹. Again, it is interesting to note that our SEP of 6.5 kg N ha⁻¹ is actually lower than the 15.7 kg N ha⁻¹ reported by Börjesson et al. (1999). In our opinion, this is a powerful illustration of why SEP values in these type of studies are often more insightful than correlation coefficients. It is possible that the unique nutrient cycling processes of flooded soils may prohibit the use of IR spectrometry for predicting N processes in soil and crop. However, this conclusion cannot be drawn with certainty from our data. A similar argument might be made for the variability in yield and biomass.

The r^2 value of 0.55 for weed biomass using NIR seems spurious, since this is higher than for any of the crop variables. However, this high value is probably an indirect effect of poor soil fertility in parts of the unfertilized transect. Weeds can be more competitive than rice under low soil fertility, and the high correlation might be linked to soil N, P and Ca/Mg status. In this respect, it is interesting to note that the correlation spectra of mineralizable N and weed biomass are largely similar (Figure 5). Also, it should be noted that this predictive power for weed biomass is, at best, relative, since it will strongly depend on pesticide applications by the farmer.

Most impressive are the r^2 values for eCEC, Ca, Mg and their ratio (Figure 3). This might be partly due to the leveling of the field for rice cultivation purposes. Since the field was originally very slightly sloping, leveling exposed the subsoil in parts of the field. At these sites, higher cation concentrations may correlate with soil color (organic matter content or small texture changes). However, it remains remarkable that this results in such a high predictive power. For the NIR they are higher than those reported by Chang et al. (2001). This may have interesting prospects for predicting and combating grass tetany. This serious cattle disease is induced by low Ca and Mg concentrations in forage (Lewis and Sparrow, 1991; Reinbott and Blevins, 1991). However, it remains to be seen whether the predictive power of NIR spectroscopy with PLSr holds up in other study areas more relevant to forage production.

Implications for use in site-specific management

It is clear from this study that NIR performs better in terms of predictive power than DRIFT-MIR. The r^2 values of 0.83, 0.82 and 0.71 for eCEC, Mg and P are considerably higher than the corresponding numbers of 0.56, 0.61 and 0.55 for DRIFT-MIR. In terms of

prediction error, this corresponds to an improvement of approximately 30% for NIR. Combined with the more complicated sample preparation and the more expensive equipment for DRIFT-MIR, and the possibilities for installing NIR sensors on farm equipment (Ehsani et al., 1999), NIR spectrometry is preferred.

As noted above, the low prediction accuracy for most crop parameters and soil total C and N might be due to the relatively small variation in these parameters within our study area. Since our prediction error for total soil N and N uptake was similar or lower than those reported, differences in these parameters in our fields may simply be below the detection limits for IR spectrometry. This could have important consequences for its use in SSM.

However, the significant results for Ca, Mg, eCEC and P Olsen certainly warrant the use of IR spectrometry in SSM. In this respect, it is important to stress that predictive models built with PLSr are unique to the area on which they were calibrated. Texture, mineralogical composition, organic matter content and other variables all strongly influence the reflectance spectra, and will therefore have an effect on the optimal model parameters. For example, Ben-Dor and Banin (1995) reported 2333, 2097 and 1431 nm as the most important wavelengths for predicting CEC. In our case, the most important wavelenghts are around 900, 2420 and 2290 nm. For effective use in precision agriculture, PLSr models need to be calibrated for the area over which they will be used. However, it is expected that, once calibrated, these models can be used for predictions over different growing seasons.

Conclusions

Both NIR and DRIFT-MIR spectrometry, combined with PLSr modeling, could simultaneously predict a range of soil and crop properties under conditions typical for precision agriculture (i.e. relatively minor variations within a field). Compared to other studies, we had low correlation coefficients but very good SEP's. This indicates that variation within a field might be to small to be detected precisely by IR spectrometry for some properties. It also illustrates that correlation coefficients are of limited value in describing the accuracy of such predictive models. In our study area, NIR performed better, with r^2 values higher than 0.90 for eCEC and basic cations higher than 0.80. NIR spectrometry, especially implemented as a sensor in farm equipment for on-the-go analysis, offers considerable perspective in precision agriculture for instantaneous, simultaneous and inexpensive prediction of a variety of soil and crop parameters. PLSr models need to be built using a calibration set specific to the research area in order to yield reliable predictions. In addition, the accuracy of predicting different properties will vary from area to area. As NIR was able to predict Ca, Mg and their ratio effectively, an exciting application might be in prediction of grass tetany in cattle.

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