Total nitrogen in rice paddy field independently predicted from soil carbon using Near Infrared Reflectance Spectroscopy (NIRS)

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Abstract. As nitrogen (N) is needed at the greatest amount for the plant growth, the addition of adequate amount of this nutrient in rice paddy field is one of the key factors for maximizing the rice production. Knowing the spatial soil N status in the rice field measured using conventional analysis takes time and expensive. Many previous researchers reported that near infrared spectroscopy (NIRS) was able to successfully predict soil N due to its high correlation to the soil carbon (C). The aim of this research is to test whether NIRS able to predict soil N content, independently predicted from soil C. Soil samples in 147 locations, including the coordinates, were collected in rice paddy field of Lombok Island, Indonesia. Parts of the samples were analysed in a laboratory using conventional analysis for total N and total organic C, and the other parts were scanned using near infrared spectroscopy (NIRS) for spectral data collection. A Partial Least Square Regression (PLSR) calibration model was developed using laboratory-analysed soil N (and C) data and soil spectral data. Although soil N and soil C have a poor correlation, but both can be predicted well using NIR technology, indicating the soil N was independently predicted from soil C. This finding shows that soil N content in rice paddy field of Lombok Island can be predicted and monitored by NIRS without depending on its high autocorrelation with soil C.

1. Introduction
Nitrogen (N) is the vital nutrient needed at the greatest amount for the growth and development of plant. This essential element is needed for amino and nucleic acid formation, plant tissue and cells development, chlorophyll formation, and photosynthesis process [1]. As the availability of this plant nutrient in agricultural soils is usually low, the addition via N fertilizer is commonly conducted in order to avoid its deficiency in soil which may reduce plant performance and yield [2]. Because most of nitrogen in soil is in organic forms, so the presence of nitrogen in soil is usually associated to the presence of soil organic matter [3]. The variety of soil N content which is highly correlated with the variety of soil organic matter content has been reported by many workers e.g. [4]. The presence of N in...
soil is not only affected by N fertilizer and soil organic matter, but also by the fixation of N2 by plant-associated bacteria [5]. Kjeldhal method is usually used to measure the total N in soil [1]. As this wet combustion technique is a tedious procedure and needs chemical reagents, scientists have developed automated dry combustion methods (e.g. LECO FP-200 CNS analyser [6] and vario MACRO cube CHNS elemental analyser [7]) which is a faster procedure. However, both methods still need sample preparation and are considered not a cheap technique. To overcome this challenge, sensor technology (e.g. near infrared spectroscopy - NIRS) has been developed which works based on the interaction of material and light [8]. This instrument doesn’t need chemical reagents and may work with little or no sample preparation. It works based on the vibration of covalent bonds of small atoms such as C-H, O-H, and N-H of the object properties [8].

The successful prediction of soil N using NIRS has been reported by many workers e.g. [9,10]. The success of C prediction was reported along with soil N and/or with other soil chemical and physical properties, such as soil P and K [11], soil bulk density [12] and soil texture [13]. As N absorbers are difficult to assign in a NIR region, some workers believe that the success of N prediction was due to its strong correlation with soil C prediction [6]. Strong correlation of soil N and C was used by Reeves III and McCarty as the reason of why soil N can be predicted by NIRS [14]. This reason was also used by Stafford et. al. when they were able to predict cadmium concentration in soil by NIRS [15], but it has strong correlation with soil C. In contrast, Chang and Laird found poor correlation between laboratory data of total N and C, but they were able to predict soil N using NIRS [9].

As papers which reported independent NIRS prediction of soil N to the soil C are still rare, in this paper it is tested the ability of NIRS to independently predict soil N to the soil C in rice paddy field of Lombok Island, Indonesia, which may be useful for monitoring the change of soil N in the soil.

2. Materials and methods

2.1. Soil sample and coordinates collection, soil analysis and spectral data pre-processing

The coordinates of 147 sample positions were determined in a map of rice paddy field of Lombok Island Indonesia. The positions were different from the locations of samples collected by Kusumo et. al. [16]. The soil samples (0-10 cm depth) were collected using soil corer (2.54 cm diameter), which then were dried, ground and sieved (with 0.2 mm diameter sieve). Parts of the samples were analysed for total N (Kjeldahl) and total organic C (Walkley and Black), and the other parts were scanned using near infrared spectroscopy (NIRFlex N500, manufactured by BÜCHI Labortechnik AG, Switzerland). The spectral data (1000-2500 nm) were pre-processed [17] (transformation to log (1/R) - R, wavelet detrending, Savitzky-Golay smoothing, first derivative, and mean centering) using ParLeS [18] for improving the robustness of the calibration model.

2.2. Developing the calibration models

Calibration models were developed using Partial Least Square Regression (PLSR) between pre-processed spectral data and laboratory analysed soil N and C data. The number of factors used to build the calibration model were determined from the model that produces the lowest root mean square error (RMSE) [18]. The best model chosen is the model that produces the highest coefficient determination (R²), the highest RPD (ratio of prediction to deviation; SD/RMSE) and the lowest RMSE (root mean square error) of measured and predicted soil N and C [19].

3. Results and discussion

3.1. Soil nitrogen and carbon content of rice paddy field

The soil N and C data which were analyzed using conventional methods were presented at table 1. Total N concentration on rice paddy field of Lombok Island varies from very low to medium, with low concentration in average. Of the total soil samples, there were 94% of the samples categorized into very
low to low concentration, and 6% was classified into medium concentration. While, 85% samples were classified into very low to low C concentration, and 14% and 1% samples were medium and high C concentration, respectively.

Table 1. Soil property of rice paddy field of Lombok Island.

| Soil property | Range | Median | Mean | Variance | Standard deviation |
|---------------|-------|--------|------|----------|--------------------|
|               | Min.  | Max.   |      |          |                    |
| N total (%)   | 0.04  | 0.28   | 0.12 | 0.11     | 0.05               |
| C total (%)   | 0.55  | 3.32   | 1.50 | 1.43     | 0.50               |

The majority of low concentration of soil N in rice paddy field of Lombok Island may be related to the low concentration of organic matter in the soil, which is probably because of (i) small amount (and/or low quality) of organic waste returned to the soil [20, and/or (ii) low input of organic or nitrogen fertilizer [20,21]. As reported by Beltrán et. al. [22], crop residues left in soil, such as leaves, twigs and roots of cover crops, contribute to the content of N in soil. Besides that, N concentration in soil may be also influenced by N-fixing bacteria, symbiotically live in the legume plant roots [23].

3.2. Relationship between laboratory analysis of soil N and C

The relationship between laboratory analysis of soil N and C concentration in rice paddy field of Lombok Island is depicted at figure 1. Poor correlation ($r = 0.60$) between soil N and C concentration indicates that the variation of N content in the soil is not entirely determined by the variation of soil organic matter content. It seems that other possible factors such additional N through fertilizer addition and or possible occurrence of N-fixing bacteria may also contribute to the variation of N content in soil [23]. The residue of N fertilizer prior the soil the soil sample collection is possibly the cause of this phenomenon, as the samples collected after harvesting the rice. Poor correlation between soil N and C concentration was also reported by Chang and Laird in the locations covered by grass, corn and soybean [9]. In contrast to this, other workers [24] reported high correlation between soil C and N concentration, in a farm covered by corn.

![Figure 1](image)

Figure 1. Relationship between soil N and C concentration.

3.3. The accuracy of NIRS prediction

The accuracy of NIRS to predict soil N and C is presented at Table 3. Both soil N and C can be predicted with moderate accuracy as shown by $R^2 0.79$ and RPD around 2.00. This moderate accuracy is in line with accuracy classification used by Chang et. al. due to the $R^2$ value between 0.5 and 0.8 and the RPD between 1.4 and 2.0 [25]. This is also in agreement with accuracy classification used by Malley et. al. due to the $R^2$ value between 0.7 and 0.8, and the RPD between 1.75 and 2.25 [26].
Table 2. Prediction values of soil N and C using leave-one-out cross-validation.

| Properties   | Prediction values (leave-one-out cross-validation) |          |          |          |
|--------------|----------------------------------------------------|----------|----------|----------|
|              | $R^2_{CV}$  | RMSE$_{CV}$ | RPD$_{CV}$ |          |
| N Total      | 0.787      | 0.023       | 2.17      |          |
| C organic    | 0.798      | 0.228       | 2.22      |          |

The relationship between soil N and C data measured by conventional analysis and predicted by NIRS is shown at Figure 2. Moderate accuracy of soil N and C predicted using NIRS indicates that this technology can be used to rapidly and efficiently measure both soil N and C in rice paddy field of Lombok Island. Successful prediction of either soil N or C using NIRS was also reported previously using tropical climate soils [16,19,27] and subtropical soils e.g. [28].

3.4. PLSR coefficient indicating independent N prediction

Partial least square regression (PLSR) coefficients for predicting soil C (blue line) and N (red line) are presented in Figure 3. Independent prediction of soil N from soil C is shown by different datasets of PLSR coefficients of soil N and C (with low correlation between PLSR coefficients of soil N and C; $r = 0.20$), which are obviously shown by different shapes of PLSR coefficients of N prediction to the C prediction model. Low correlation between PLSR coefficients of soil N and C can also be used to indicate independent prediction of soil N from soil C. Kusumo et. al. [24] previously used PLSR coefficients to notice independent NIRS prediction of maize root density from soil C and N.

Figure 2. Relationship between laboratory and NIRS analysis of soil N and C.

Figure 3. PLSR coefficient for soil C and N prediction.

Independent prediction of soil N from soil C can also be explained from the poor autocorrelation ($r = 0.60; R^2 = 0.35$) between laboratory analysis of soil C and N data (Figure 1), which is far lower than the correlation ($R^2 = 0.79$) between soil N measured in laboratory and predicted by NIRS (Figure 2a). This reason was also used by Chang and Laird [9] who found poor autocorrelation ($R^2 = 0.49$) between laboratory data of total N and C, but they were able to predict soil N using NIRS with high correlation ($R^2 = 0.97$) between total N measured in laboratory and predicted by NIRS (cross validation).
In spite of that, PLSR regression coefficients can also be used to explain the important bands in explaining the variance of soil N and C (Figure 3). Bands which have larger coefficient size (positive or negative) represent to be more important in explaining the variance of soil N and C, compared to the bands with smaller coefficient. This also has been used by previous workers in determining the important bands for soil C and N prediction [6, 24].

4. Conclusion
Total soil N concentrations in rice paddy field of Lombok Island Indonesia vary from very low to medium, with the majority of low content. This is similar to the status of total soil C. Near infrared technology was moderately successful to measure both soil N and C in the study area. Low correlation between PLSR coefficients of soil N and C concludes that soil N is independently predicted from soil C. This also can be seen from low correlation between laboratory analysis of soil C and N data, but there is high correlation between soil N measured in laboratory and predicted by NIRS. This indicates that soil N content in rice paddy field of Lombok Island can be monitored by NIRS without depending on its correlation to the soil C. This technology may be further used for mapping the soil N status in the study area and the map may be further used as a guidance for fertilizer application.

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References
[1] Barker A V and Pilbeam D J (Eds.) 2015 Handbook of plant nutrition (CRC press)
[2] Choudhury A T M A and Kennedy I R 2005 Nitrogen fertilizer losses from rice soils and control of environmental pollution problems Communications in Soil Science and Plant Analysis 36 (11-12) 1625-1639
[3] Knops J M and Tilman D 2000 Dynamics of soil nitrogen and carbon accumulation for 61 years after agricultural abandonment Ecology 81(1) 88-98
[4] Weintraub M N and Schimel J P 2003 Interactions between carbon and nitrogen mineralization and soil organic matter chemistry in arctic tundra soils Ecosystems 6(2) 0129-0143
[5] Regan K, Stempflhuber B, Schloter M, Rasche F, Prati D, Philippot L and Marhan S 2017 Spatial and temporal dynamics of nitrogen fixing, nitrifying and denitrifying microbes in an unfertilized grassland soil Soil Biology and Biochemistry 109 214-226
[6] Kusumo B H, Hedley C B, Hedley M J, Hueni A, Tuohy M P and Arnold G C 2008 The use of diffuse reflectance spectroscopy for in situ carbon and nitrogen analysis of pastoral soils Australian Journal of Soil Research 46 623-35
[7] Calvelo Pereira R, Hedley M, Camps Arbeastain M, Wismubroto E, Green S, Sagar S, Kusumo B H and Mahmud A F 2016 Net changes of soil C stocks in two grassland soils 26 months after simulated pasture renovation including biochar addition GCB Bioenergy 8(3) 600-615
[8] Stenberg B, Viscarra Rossel R A, Mouazen A M and Wetterlind J 2010 Chapter Five-Visible and Near Infrared Spectroscopy in Soil Science Advances in Agronomy 107 163-215
[9] Chang C W and Laird D A 2010 Chapter Five-Visible and Near Infrared Spectroscopy in Soil Science Advances in Agronomy 107 163-215
[10] Sithole N J, Ncama K and Magwaza L S 2018 Robust Vis-NIRS models for rapid assessment of soil organic carbon and nitrogen in Feralsols Haplic soils from different tillage management practices Computers and electronics in agriculture 153 295-301
[11] Carra J B, Fabris M, Dieckow J, Brito O R, Vendrame P R S and Macedo Dos Santos Tonial L 2019 Near-Infrared Spectroscopy Coupled with Chemometrics Tools: A Rapid and Non-
Destructive Alternative on Soil Evaluation Communications in Soil Science and Plant Analysis 50(4) 421-434

[12] Roudier P, Hedley C B and Ross C W 2015 Prediction of volumetric soil organic carbon from field-moist intact soil cores European Journal of Soil Science 66(4) 651-660

[13] Jaconi A, Vos C and Don A 2019 Near infrared spectroscopy as an easy and precise method to estimate soil texture Geoderma 337 906-913

[14] Reeves III JB and McCarty GW 2000 The potential of near infrared reflectance spectroscopy as a tool for spatial mapping of soil composition for use in precision agriculture. In 'Near Infrared Spectroscopy: Proceeding of the 9th International Conference'. Norwich UK (Eds Davies AMC and Giangiacoomo R) p 587-591

[15] Stafford A D, Kusumo B H, Jeyakumar P, Hedley M J and Anderson C W 2018 Cadmium in soils under pasture predicted by soil spectral reflectance on two dairy farms in New Zealand Geoderma regional 13 26-34.

[16] Kusumo B H, Sukartono S and Bustan B 2018 Rapid Measurement of Soil Carbon in Rice Paddy Field of Lombok Island Indonesia Using Near Infrared Technology In IOP Conference Series: Materials Science and Engineering 306(1) 012014

[17] Kusumo B H, Arbestain M C, Mahmud A F, Hedley M J, Hedley C B, Pereira R C, Wang T and Singh B P 2014 Assessing biochar stability indices using near infrared spectroscopy Journal of Near Infrared Spectroscopy 22(5) 313-328

[18] Viscarra Rossel R A 2008 ParLeS: Software for chemometric analysis of spectroscopic data Chemometrics and Intelligent Laboratory Systems 90 72-83

[19] Kusumo B H 2018 The rapid measurement of soil carbon stock using near-infrared technology In IOP Conference Series: Earth and Environmental Science 129(1) 012023

[20] Córdova S C, Olk D C, Dietzel R N, Mueller K E, Archontoulis S V and Castellano M J 2018 Plant litter quality affects the accumulation rate, composition, and stability of mineral- associated soil organic matter Soil Biology and Biochemistry 125 115-124

[21] Hijbeek R, Ten Berge H F M, Whitmore A P, Barkusky D, Schröder J J and Van Ittersum M K 2018 Nitrogen fertiliser replacement values for organic amendments appear to increase with N application rates Nutrient cycling in agroecosystems 110(1) 105-115

[22] Beltrán M J, Sainz-Rozas H, Galantini J A, Romaniuk R I and Barbieri P 2018 Cover crops in the Southeastern region of Buenos Aires, Argentina: effects on organic matter physical fractions and nutrient availability Environmental Earth Sciences 77(12) 428

[23] Kuypers M M, Marchant H K and Kartal B 2018 The microbial nitrogen-cycling network Nature Reviews Microbiology 16(5) 263

[24] Kusumo B H, Hedley M J, Hedley C B and Tuohy M P 2011 Measuring carbon dynamics in field soils using soil spectral reflectance: prediction of maize root density, soil organic carbon and nitrogen content Plant and Soil 338(1-2) 233-45

[25] Chang C W, Laird D A, Mausbach M J and Hurburg C R J 2001 Near-infrared reflectance spectroscopy – principal component regression analysis of soil properties Soil Science Society of America Journal 65 480-490

[26] Malley D F, Martin P D and Ben-Dor E 2004 Application in analysis of soils Near-Infrared Spectroscopy in Agriculture, Agronomy Monograph no. 44. 'ed Barbarick K A, Roberts C A, Dick W A et al (Madison, Wisconsin, USA: American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc.) pp 729-84

[27] Barthès B G, Kouakoua E, Clairotte J, Lallemand J, Chapuis-Lardy L, Rabenarivo M and Roussel S 2019 Performance comparison between a miniaturized and a conventional near infrared reflectance (NIR) spectrometer for characterizing soil carbon and nitrogen Geoderma 338 422-429

[28] Sorenson P T, Quideau S A and Rivard B 2018 High resolution measurement of soil organic carbon and total nitrogen with laboratory imaging spectroscopy Geoderma 315 170-177