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# Rapid Estimation of Wheat Straw Decomposition Constituents Using Near-Infrared Spectroscopy

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**Abstract:** Adoption of no-till systems in Eastern Washington has been slow due to the difficulty of managing wheat (*Triticum aestivum* L.) straw residue and the unknown decomposition potential of cultivars. We hypothesize that by analyzing wheat straw with near-infrared spectroscopy (NIRS), calibration models can be developed to accurately predict fiber and chemical constituents of wheat, determining straw decomposition potential. Straw from a panel of 480 soft winter wheat cultivars adapted to the Pacific Northwest are analyzed for neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL), cellulose, hemicellulose, carbon (C), and nitrogen (N). Using modified partial least squares regression and cross validation techniques, specific environment and broad-based NIRS models are calibrated and predictive ability is validated. $R^2_{cal}$ values from broad models are better than the specific models, and are 0.85 (NDF), 0.86 (ADF), 0.65 (ADL), 0.88 (cellulose), 0.42 (hemicellulose), 0.67 (C), and 0.73 (N). The corresponding SEP values are 1.68% (NDF), 1.54% (ADF), 0.62% (ADL), 1.14% (cellulose), 1.11% (hemicellulose), 1.23% (C), and 0.06% (N). A Finch × Eltan breeding population is used to further validate models and prediction accuracies for variety selection within a breeding program scenario. The broad NIRS models prove useful for estimating high and low ranges of NDF, ADF, and cellulose in wheat cultivars which translate into characteristics of slow and fast decomposition potential.

**Keywords:** decomposition; wheat; straw; near-infrared spectroscopy; NIRS; NDF; ADF; ADL

## 1. Introduction

The rainfed regions of Eastern Washington are recognized for their highly successful dryland wheat (*Triticum aestivum* L.) production systems. However, soil erosion threatens the future productive stability of these cropping systems [1,2]. In regions receiving high precipitation (>300 mm), annual cropping is generally practiced with a three-year rotation of winter wheat/spring cereal/spring legume [3]. These regions are distinguished by slopes as steep as 45% [4] and soils high in clay content [3]. Conventional tillage practices are common and can accelerate erosion issues [5]. The combination of steep slopes, clay soils, and tillage makes these cropping systems prone to serious water erosion [3,6]. Water erosion is especially serious on newly planted winter wheat following a low-residue spring legume [3].

In contrast, the production regions of central Washington receive less than 300 mm of annual precipitation and the grain yield potential is low [3]. Due to the low amount of annual precipitation, a regularly practiced winter wheat/summer fallow cropping system is used, intended to conserve moisture [7]. This rotation involves a 13-month period of barren soil between the harvest and planting of wheat [8] that allows the soil to store water. Tillage is conducted during summer months to break the capillary pores in the soil and it creates a soft dust mulch, which minimizes water losses due to

evaporation [9]. Unfortunately, this practice produces fine particulate matter ≤10 µm in diameter (PM10) which are prone to intense wind erosion [10]. This is the dominant rotation in the low precipitation region because no other system has proven able to compete agronomically or economically [11].

Leaving straw residue on top of the soil through reduced tillage or through planting directly into the stubble of the previous crop (colloquially termed 'no-till') is an excellent solution to minimize soil erosion in both high and low rainfall regions of Eastern Washington. Accumulated runoff and soil erosion have been observed to be up to 54 times lower in a no-till system than in a conventional tillage system [5]. Long term benefits in soil quality have been observed in no-till systems [4]. Excessive surface residue can, however, create difficulties in planting and can delay seed germination [12]. Seeding into a no-till field is often only possible for farmers who can afford to invest in specialized planting equipment designed for this purpose [13]. Many growers resort to alternative management practices for straw which can be detrimental to air and soil quality, such as burning or baling [14,15]. Managing straw residue in sustainable ways will be important for continued production of wheat in the Pacific Northwest while minimizing soil erosion.

Depending on the cropping system each grower is using, the needs for straw residue management will differ. Within no-till production systems in high rainfall regions, straw will need to decompose rapidly over the winter months to avoid the planting complications that excessive straw residue can create in the spring. On the other hand, straw residue in the low rainfall regions needs to decompose slowly to cover the soil during the entirety of the fallow season. Wheat fiber and chemical constituents have previously been associated with straw decomposition [16,17]. The standard method for determining decomposition potential in winter wheat is based upon a fiber and nutrient analysis [18] that quantifies hemicellulose, cellulose, and acid detergent lignin (ADL) through a wet chemistry process that measures neutral detergent fiber (NDF), acid detergent fiber (ADF), and ADL. Nitrogen (N), carbon (C), and C:N ratios are analyzed in straw by dry combustion and are also used to determine decomposition [19]. High NDF, ADF, ADL, and low N are all indicators of slow decomposition [16]. However, these fiber and chemical analysis methods are slow, expensive, and destructive to the samples.

Near-infrared spectroscopy (NIRS) is potentially an inexpensive, rapid, and nondestructive method for predicting fiber and nutrient content of wheat residue. Prediction models can be made by developing a partial least squares regression to predict phenotypic data based on NIRS- generated spectra. In wheat, NIRS calibration models have been successful for determining protein and gluten content [20,21]. NIRS has also been evaluated to predict the degradability and ash content of wheat straw for use in bioethanol production [22]. Furthermore, wheat and rice straw has been evaluated for use in energy conversion, with NIRS being tested as a predictive measure [23]. The ruminal animal industry has successfully used NIRS to determine chemical composition and nutritive value of forages and straw [24,25]. NIRS also successfully predicted NDF, ADF, and N in canola [26], NDF and ADF in dryland cereal cultivars [14], and ADF and ADL in rice [27]. The use of NIRS is routine for prediction of various traits in many other agricultural crops such as postharvest quality of apples [28], postharvest ripeness and quality of mango [29,30], and carbohydrate content in zucchini fruit [31].

The objective of this experiment was to analyze a diverse winter wheat population with NIRS to develop prediction models that would facilitate the determination of residue decomposition rates. By standardizing NIRS as a primary method of predicting residue decomposition rates, breeders will be able to select for this trait in their breeding programs and farmers can be provided with information regarding the decomposition potential of released winter wheat cultivars. The risk involved with transitioning to no-till systems will be reduced because farmers will be able to make informed decisions when selecting a cultivar that meets their specific needs for production.

## 2. Materials and Methods

### *2.1. Sample Collection and Preparation*

Two separate populations were used in this study. The first was a panel of 480 advanced soft white winter wheat cultivars from breeding programs in the Pacific Northwest (Washington State

University, University of Idaho, Oregon State University, USDA-ARS). This panel was harvested from Pullman, WA in 2016 and from Pullman, Central Ferry, and Mansfield, WA in 2017. Pullman is located at 46.73° N, 117.18° W, on the eastern border of Washington state at 717 m elevation above sea level. The average annual precipitation exceeds 500 mm, soil types range from silt loams to silty clay loams [32], and winter wheat grain yields average 7900 kg/ha [33]. Central Ferry is located approximately 95 km southwest of Pullman at 46.62° N, 117.79° W and 195 m elevation. Central Ferry averages approximately 6700 kg/ha of grain yield under irrigation (600 mm) on silt loam soils [32]. Mansfield, located 320 km northwest of Pullman at 47.81° N, 119.64° W, has an annual precipitation of less than 300 mm and grain yields average around 3550 kg/ha [33]. The soils are classified as ashy fine sandy loam [32] and the elevation is 692 m. At each location, the population and checks were planted in an augmented design with repeating checks every 20 entries and one rep per location. The second population included 167 recombinant inbred lines (RIL) developed through single seed descent after crossing Finch (PI 628640) and Eltan (PI 536994) winter wheat cultivars [34–36]. These two cultivars were selected for crossing because they are cultivars released for production in the low rainfall areas of Washington and stark contrasts in decomposition potential exist between the two [16]. This population was harvested from Pullman, Mansfield, and Waterville, WA in 2015, whereas samples were harvested in 2017 from Pullman and Mansfield. Waterville is located approximately 50 km southwest of Mansfield, has mostly silty loam and sandy loam soils [32], and has grain yields comparable to Mansfield. The coordinates of Waterville are 47.65° N, 120.07° W and the elevation is 800 m. At all locations, the Finch/Eltan RIL population was planted as a randomized complete block with two reps per location and a repeating check every 20 entries. In all experiments 0.5 m rows of straw from each plot was cut just above ground level at harvest maturity (Stage 11.4 on Feekes' scale) [37,38] and placed in brown paper sacks with the grain removed. For consistency, the leaves and the nodes were removed, leaving only the internode portion of the straw. The internode residue was cut into 1–2 cm pieces and then ground to pass through a one mm sieve using a FOSS Cyclotec Sample Mill (FOSS North America, Eden Prairie, MN, USA). Samples were stored in a low humidity chamber prior to analysis to ensure similar moisture content.

### 2.2. Fiber and Nutrient Analysis

Neutral detergent fiber, ADF, and ADL were determined by analyzing 0.5–0.55 gram of ground winter wheat straw using the vanSoest et al. [18] procedure modified slightly by using an ANKOM automated system with specialized filter bags (ANKOM Technology, Macedon, NY, USA). The NDF procedure removed starches, sugars, free amino acids, and other water-soluble components, leaving hemicellulose, cellulose, and ADL. The ADF procedure removed the hemicelluloses, leaving only the cellulose and ADL. The ADL procedure removed the cellulose from the straw. The NDF and ADF procedures were performed sequentially using an ANKOM 200 Fiber Analyzer (ANKOM Technology, Macedon, NY, USA). The straw samples were then digested in 72% $H_2SO_4$ to determine the ADL. After each procedure, the samples were dried overnight in a fume hood and then were oven dried in a hybridization incubator for a minimum of 6 h at 64 °C. The samples were removed from the incubator, placed in desiccator pouches to cool, and individually weighed. The hemicellulose value was calculated as the difference between NDF and ADF whereas the cellulose value was determined by calculating the difference between ADF and ADL. Carbon and N were determined using dry combustion with a LECO TruSpec Analyzer (LECO Corp., St. Joseph, MI, USA) as described by Gazulla et al. [39].

### 2.3. Near-Infrared Spectroscopy

Finely ground winter wheat residue from the internode samples described above was enclosed in metal ring cups (36 mm inside diameter) and scanned with a FOSS XDS Rapid Content Analyzer (FOSS North America, Eden Prairie, MN, USA) using ISIscan software, version 3.10 (Infrasoft International, State College, PA, USA). At the start of each day, check samples were run to calibrate the machine. Each sample was then scanned twice, with the cup rotated 90° between the first and second scan, using the wavelength range 400–2498 nm at 2 nm

intervals. The two resulting spectra from each sample were averaged. Background spectra was recorded with each sample analyzed.

### *2.4. Statistics*

The data from each of the four environments from the first population of 480 cultivars were combined into one set to develop broad range prediction models for each trait, with the exception of one cultivar which was removed from analysis due to lack of emergence under field conditions. After laboratory reference data was combined with the corresponding spectra, each data set was randomly divided into two parts to develop calibration models ($n$ = 1566) and to validate the models ($n$ = 350) using WinISI software, version 4.0 (Infrasoft International, State College, PA, USA). Roughly 18% of the samples were used in the validation models using a random selection procedure within the WinISI software. Principle component analysis was used to eliminate spectral outliers, which were defined as spectra with Mahalanobis distance values greater than 3.0. Modified partial least-squares (MPLS) and fold-cross validation methods using four iterations, as implemented in the WinISI software, were used to develop prediction models [40]. The modification to PLS scales the reference method data and the reflectance data at each wavelength to ensure a standard deviation (SD) of 1.0 before each PLS term [40]. Standard normal variant and detrend (SNV-D) as a scatter correction, first and second derivative spectra, as well as mathematical treatments for derivative order number, gap, first smoothing, and second smoothing were applied. The derivative order improved spectral resolution by enhancing spectral differences [41,42]. The gap (listed as the second value in the math treatment) was the length in nm between points over which the derivative was calculated and the smoothing treatments were used to reduce random noise in the spectral data [42]. The degree of first smoothing is expressed by the segment of wavelength points used as a moving average to 'smooth' the spectral output, and the number of wavelength points used is listed as the third value in the math treatment. For all models, the second smoothing (fourth value in the math treatment) was set at 1 to indicate that no second smoothing was used. Numerous combinations of math treatments were tested to develop prediction models. The best prediction equation was determined by identifying that which displayed the highest 1-variance ratio (1-VR) and lowest standard error of cross validation (SECV). The ratio of the SD of phenotypic data to the SECV was calculated, as done by Deaville et al. [43], to determine if an equation was acceptable for quantitative prediction, screening only, or was not useful. The standard error of the calibration (SEC) and the coefficient of determination ($R^2$) were also computed. The unit of measurement for SEC, SECV, and SEP are all recorded in percentages. The second population of RIL was used to confirm the best prediction equation performance in a breeding population closely related to the first population, and analyses were repeated as described above.

## 3. Results and Discussion

### *3.1. Calibration Models*

Summary statistics for fiber and chemical constituents from the four locations are presented in Table S1. Calibration models were developed for each trait based on the highest 1-VR and lowest SECV, after all environments were combined into one dataset. The mathematical treatments accounting for derivative, gap, and first smoothing differed for each trait when developing calibration models (Table 1). The 1-VR values were highest for NDF, ADF, and cellulose models and lowest for ADL and hemicellulose models (Table 1). SECV values ranged from 0.05% for N to 1.52% for NDF. The SD/SECV is a guideline for determining whether an equation can be validly used for making predictions, as utilized by Deaville et al. [43]. Calibrations with SD/SECV ratios >3.0 are useful for quantitative prediction, models with ratios >2.5 and <3.0 are acceptable for screening purposes, and any equation with a ratio <2.5 is not considered to be useful. A high SD indicates high variation within a population and is desirable because increased data variation will improve the robustness of a calibration [28] and result in an increased SD/SECV ratio. A low SECV indicates that the NIRS calibration is predicting

similarly during each iteration of the cross-validation process [41]. According to these guidelines, our NDF and ADF models are useful for sample screening whereas the cellulose equation is acceptable for quantitative prediction (Table 1).

**Table 1.** Near-infrared spectroscopy (NIRS) calibration statistics of the broad models developed when combining a population of 480 cultivars in four environments.

| Trait | Math Treatment | *n* | Mean | SD | SEC (%) | $R^2_{cal}$ | SECV (%) | 1-VR | SD/SECV |
|---|---|---|---|---|---|---|---|---|---|
| NDF | 2,6,4,1 | 1517 | 79.48 | 4.12 | 1.49 | 0.87 | 1.52 | 0.86 | 2.71 |
| ADF | 2,6,4,1 | 1511 | 51.79 | 3.92 | 1.32 | 0.89 | 1.38 | 0.88 | 2.84 |
| ADL | 1,10,10,1 | 1504 | 6.42 | 0.97 | 0.55 | 0.68 | 0.56 | 0.67 | 1.73 |
| CELL | 2,6,4,1 | 1513 | 45.34 | 3.17 | 0.97 | 0.91 | 1.00 | 0.90 | 3.17 |
| HEMI | 2,10,10,1 | 1513 | 27.63 | 1.43 | 1.06 | 0.45 | 1.07 | 0.44 | 1.34 |
| C | 3,5,5,1 | 1508 | 43.32 | 2.19 | 1.08 | 0.76 | 1.12 | 0.74 | 1.96 |
| N | 2,4,4,1 | 1511 | 0.16 | 0.10 | 0.05 | 0.75 | 0.05 | 0.73 | 2.00 |

SNV and detrend was used for scatter correction. For traits, NDF is neutral detergent fiber, ADF is acid detergent fiber, ADL is acid detergent lignin, CELL is cellulose, HEMI is hemicellulose, C is carbon, N is nitrogen. The four numbers listed for each trait under Math Treatment are sequentially: derivative number, gap, first smoothing, second smoothing. *n* is number of samples in calibration set; SD is standard deviation; SEC is standard error of calibration; $R^2_{cal}$ is coefficient of determination; SECV is standard error of cross validation; 1-VR is 1 minus the variance ratio; SD/SECV is ratio of standard deviation to standard error of cross validation.

Initially, individual calibration models were developed for each separate environment (Table S2). The 1-VR for NDF was best in Pullman 2016, best in Central Ferry 2017 for ADF, and moderately high across all environments for cellulose. However, the SD/SECV ratio threshold for acceptable performance was not met for the individual environment calibrations. Due to the decreased number of data points and variability within the populations, the individual environment calibration models were much poorer in comparison to the combined environment models (Table 1; Table S2). A broad-based NIRS calibration has advantages over specific calibrations within environments, with increased reliability and robustness [44].

### 3.2. Validation of Models

The best combined environment calibration models were used to predict a randomly selected validation set ($n$ = 350) that was removed from the population prior to equation development (Table 2). Cellulose was predicted with the highest accuracy and the predictions for ADF and NDF were also acceptable. Nitrogen was predicted with reasonable accuracy, although the SD/SECV ratio of the N equation was below 2.5 which indicates that the usefulness of the equation may be questionable. The $R^2_{pred}$ values for ADL and hemicellulose were lower than all other traits included in this study. Additionally, the slope of each trait neared 1 (Table 2; Figure 1).

**Table 2.** Near-infrared spectroscopy (NIRS) validation statistics displaying laboratory reference measurements vs. NIRS predicted results for the broad models and validation set.

| Laboratory Measurements | | | | | Validation Results | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Trait | *n* | Range | Lab Mean | Lab SD | NIRS Mean | Bias | $R^2_{pred}$ | SEP (%) | Slope |
| NDF | 350 | 66.64–87.21 | 78.88 | 4.38 | 79.07 | −0.196 | 0.85 | 1.68 | 1.02 |
| ADF | 349 | 40.54–60.14 | 51.47 | 4.10 | 51.52 | −0.053 | 0.86 | 1.54 | 1.03 |
| ADL | 350 | 3.91–9.21 | 6.37 | 1.05 | 6.37 | 0.005 | 0.65 | 0.62 | 1.08 |
| CELL | 349 | 35.20–51.13 | 45.09 | 3.31 | 45.12 | −0.030 | 0.88 | 1.14 | 1.02 |
| HEMI | 349 | 22.84–31.35 | 27.45 | 1.45 | 27.53 | −0.074 | 0.42 | 1.11 | 0.94 |
| C | 349 | 39.39–47.56 | 43.35 | 2.12 | 43.41 | −0.061 | 0.67 | 1.23 | 0.94 |
| N | 347 | 0.00–0.56 | 0.17 | 0.11 | 0.18 | −0.003 | 0.73 | 0.06 | 0.95 |

NDF is neutral detergent fiber, ADF is acid detergent fiber, ADL is acid detergent lignin, CELL is cellulose, HEMI is hemicellulose, C is carbon, N is nitrogen. n is number of samples in calibration set; SD is standard deviation; Bias is the difference between the mean of reference data and the mean of NIRS predicted values; $R^2_{pred}$ is coefficient of determination; SEP is standard error of prediction.

In previous literature concerning NIRS predictions of fiber characteristics in other crops, there are findings that are both similar and dissimilar to ours. Excellent NIRS prediction models were developed by Jin and Chen [45] for cellulose of rice straw and NDF and ADF of barley straw were successfully predicted by Mathison et al. [22]. Campo et al. [46] reported high $R^2_{pred}$ values for NDF (0.91) and ADF (0.91) in maize whereas Wittkop et al. [47] reported an $R^2_{pred}$ value for NDF of oilseed rape as 0.62. Several other studies that used NIRS to predict ADL in numerous grain crops reported $R^2_{pred}$ values higher than ours [27,48]. Stubbs and Kennedy [26] developed excellent calibration models for NDF, ADF, ADL, C, and N in canola and all traits, with the exception of ADL, which had models that surpassed the SD/SECV threshold of 3.0.

Correlations between reference data and NIRS predicted values for all traits were statistically significant ($p < 0.05$). Laboratory reference values and predicted values had high Pearson correlation coefficients (above 0.90) for NDF, ADF, and cellulose (Table 3). Reference and NIRS predicted values for ADL, C, and N were also moderately high, ranging from 0.81 to 0.86. The Pearson correlation coefficient was lowest for hemicellulose.

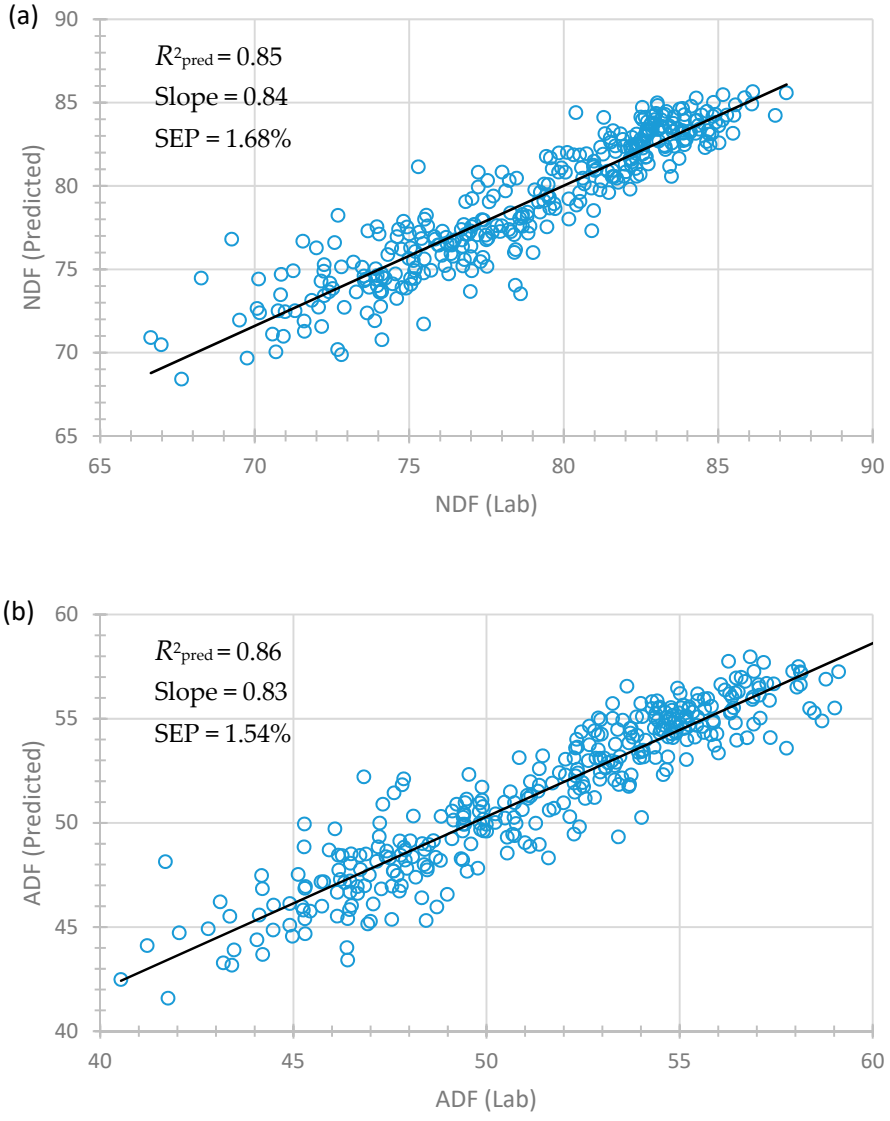


**Figure 1.** *Cont.*

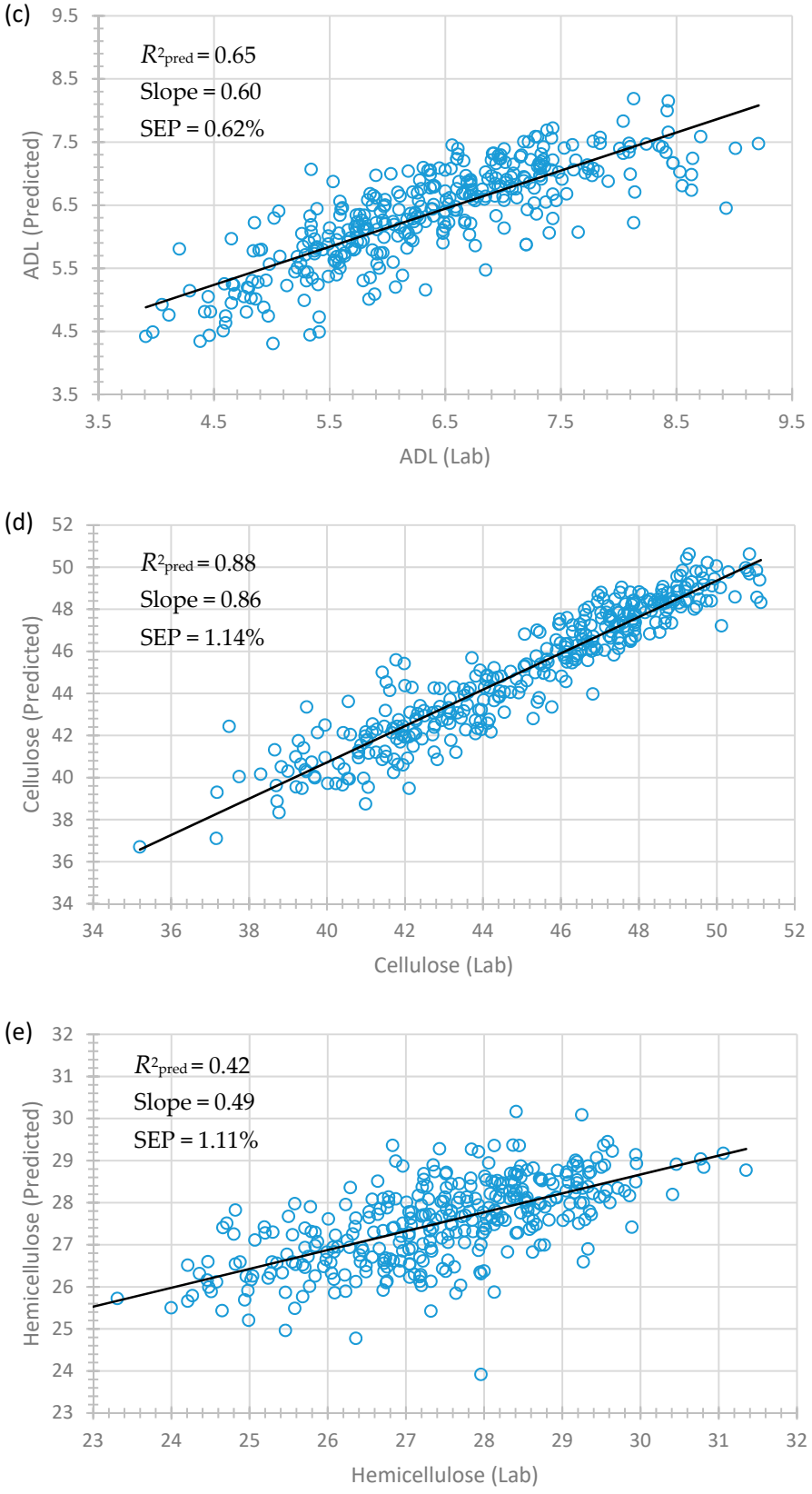


**Figure 1.** *Cont.*

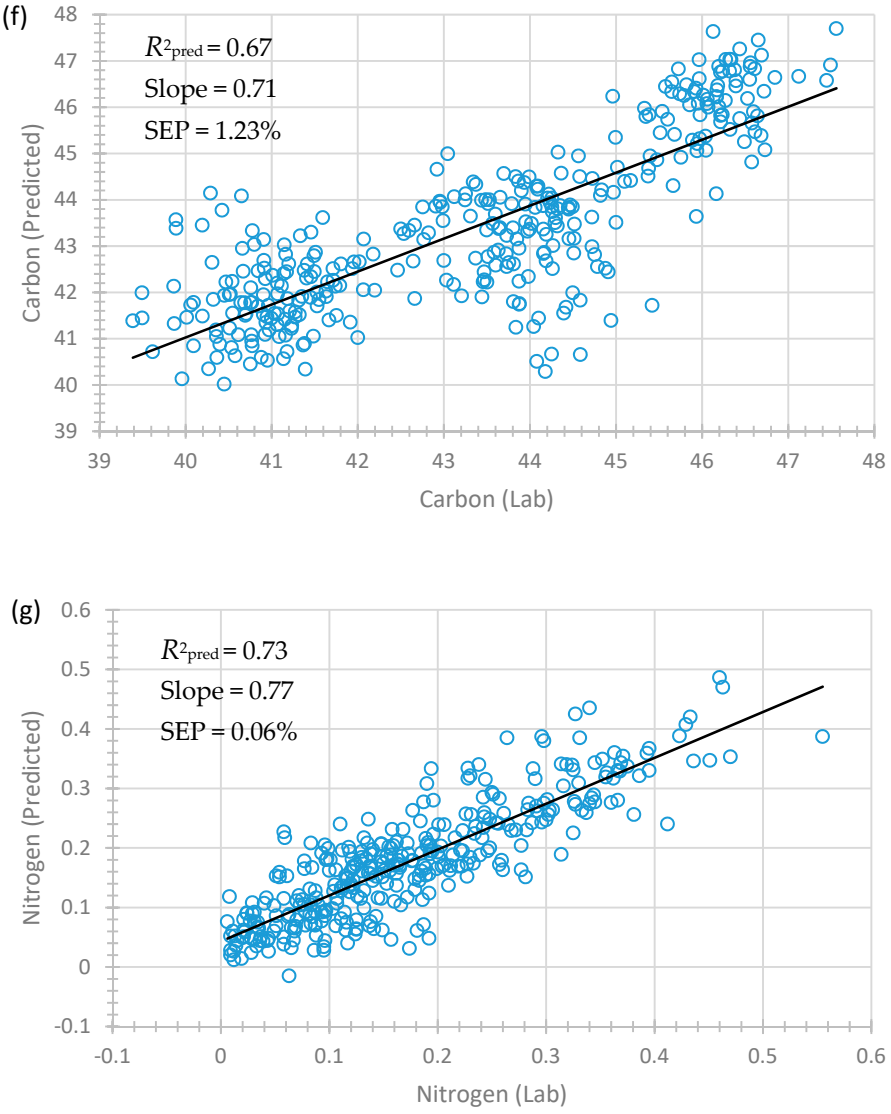


**Figure 1.** Linear regression relationship (includes $R^2_{pred}$, slope, and SEP) of laboratory reference data and NIRS predicted values from the first validation set for (**a**) neutral detergent fiber (NDF), (**b**) acid detergent fiber (ADF), (**c**) acid detergent lignin (ADL), (**d**) cellulose, (**e**) hemicellulose, (**f**) carbon, and (**g**) nitrogen using the broad NIRS models developed when combining a population of 480 cultivars in four environments.

**Table 3.** Coefficients of Pearson Correlation between laboratory reference data and NIRS predicted values for NDF, ADF, ADL, cellulose, hemicellulose, C, and N in the first validation set.

| | NDF | ADF | ADL | CELL | HEMI | C | N |
|---|---|---|---|---|---|---|---|
| Correlation | 0.92 | 0.93 | 0.81 | 0.94 | 0.65 | 0.82 | 0.86 |
| *p*-value | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |

NDF is neutral detergent fiber, ADF is acid detergent fiber, ADL is acid detergent lignin, CELL is cellulose, HEMI is hemicellulose, C is carbon, N is nitrogen. $\alpha = 0.05$ for the probability level.

Other guidelines for acceptability of NIRS predictions have been proposed besides the SD/SECV ratio. Williams [49] recommended the residual prediction deviation (RPD) guideline, which is calculated as the ratio of the standard deviation of laboratory reference values and the standard error of prediction

(SEP) of the validation set. An RPD value greater than or equal to 2.5 was considered acceptable for NIRS predictions [24], whereas an RPD of 10 or greater was considered excellent [24,49]. In our study, the RPD of NDF (2.61), ADF (2.66), and cellulose (2.90) predictions would be considered successful. The range error ratio (RER), or the ratio of the range of reference data to the SEP, was another NIRS guideline originally developed by Starr et al. [50]. Malley et al. [51] developed guidelines to use the RER alongside the $R^2_{pred}$ and RPD for additional insight into the acceptability of NIRS predictions on environmental samples. They proposed that excellent predictions have $R^2_{pred} > 0.95$, RPD > 4, and RER > 20, successful predictions have $R^2_{pred}$ between 0.90 and 0.95, RPD = 3–4, and RER = 15–20, and moderately successful predictions have $R^2_{pred}$ between 0.8 and 0.9, RPD = 2.25–3, and RER = 10–15. Moderately useful predictions have $R^2_{pred}$ from 0.7 to 0.8, RPD = 1.75–2.25, and RER = 8–10. Our predictions of NDF ($R^2_{pred}$ = 0.85, RPD = 2.61, RER = 12.24), ADF ($R^2_{pred}$ = 0.86, RPD = 2.66, RER = 12.73), and cellulose ($R^2_{pred}$ = 0.88, RPD = 2.90, RER = 13.97) would be considered moderately successful whereas the prediction for N ($R^2_{pred}$ = 0.73, RPD = 1.83, RER = 9.33) would be considered only moderately useful. Model indices for C, hemicellulose, and ADL are not reported as they did not meet the 2.5 RPD threshold for acceptable NIRS predictions.

Calibration models developed for individual environments were also used to predict validation sets that had been removed from each population before the models were created (Table S3).

Models developed for Central Ferry 2017 best predicted NDF, ADF, cellulose, and C whereas predictions for N, ADL, and hemicellulose were less accurate. For Pullman 2016, the best prediction accuracies were again observed for NDF, ADF, cellulose, and C. Hemicellulose and ADL were predicted with less accuracy, whereas the $R^2_{pred}$ value for N was the lowest for all traits in this environment. In Pullman 2017, N had a higher $R^2_{pred}$ than all other traits besides cellulose. This is contrary to what was predicted in other environments as prediction accuracies for N were generally lower than most traits. The predictions in Mansfield 2017 were similar to those of Central Ferry 2017 and Pullman 2016, with NDF, ADF, and cellulose being predicted with the highest accuracies. When compared to the $R^2_{pred}$ values from the broad calibration model predictions, each trait was predicted with less accuracy in every environment. The $R^2_{pred}$ values for C in Central Ferry 2017 and Pullman 2016 were similar to the $R^2_{pred}$ for C from the broad model, but were still slightly lower. These results demonstrated that a narrow, specific calibration will generally predict with lower accuracy than a broad, robust calibration.

### *3.3. Predictions within Breeding Populations*

Our calibration models were developed with the purpose of predicting decomposition constituents of winter wheat cultivars from a broad range of environments and germplasm. For this reason, the models were further validated by predicting NDF, ADF, ADL, cellulose, hemicellulose, C, and N of straw samples in a breeding population derived from a cross of Finch and Eltan, two winter wheat cultivars from the Pacific Northwest that were also included in the first population. Across all environments, the highest $R^2_{pred}$ values were generally found in NDF, ADF, and cellulose (Table 4). Hemicellulose was consistently difficult to predict and NIRS was generally unsuccessful in predicting C and N. Based upon $R^2_{pred}$ values, our equation best predicted NDF in Waterville 2015, ADL, hemicellulose, and C in Pullman 2015, and ADF, cellulose and N in Pullman 2017. The lowest $R^2_{pred}$ values for each trait were observed in Mansfield 2017, with the exception of N which was lowest in Waterville 2015. Like the $R^2_{pred}$ values, Pearson correlation coefficients were generally lower in this population than they were in the first validation set (Table 5). Even though these values are lower than in the original validation sets, they are expected since we are moving from a diversity panel to a breeding population. Within a breeding context, these values are still acceptable for making selections within segregating populations and identifying lines with either fast or slow decomposition potential.

**Table 4.** NIRS validation statistics for all fiber and chemical constituents in five environments from the Finch × Eltan Breeding Population.

| Lab Measurements | | | | Validation Results | | | | |
|---|---|---|---|---|---|---|---|---|
| **Trait** | ***n*** | **Lab Mean** | **Lab SD** | **NIRS Mean** | **Bias** | **$R^2_{pred}$** | **SEP (%)** | **Slope** |
| F × E Pullman 2015 | | | | | | | | |
| NDF | 142 | 86.97 | 0.83 | 85.38 | 1.587 | 0.53 | 1.71 | 0.68 |
| ADF | 142 | 59.30 | 1.18 | 56.45 | 2.854 | 0.56 | 2.96 | 0.89 |
| ADL | 142 | 10.99 | 0.63 | 7.43 | 3.552 | 0.52 | 3.58 | 0.98 |
| CELL | 142 | 48.34 | 0.80 | 48.83 | −0.497 | 0.50 | 0.77 | 0.75 |
| HEMI | 142 | 27.65 | 0.75 | 29.16 | −1.508 | 0.50 | 1.60 | 0.93 |
| C | 154 | 46.14 | 0.57 | 46.32 | −0.178 | 0.29 | 0.77 | 0.35 |
| N | 158 | 0.155 | 0.062 | 0.206 | −0.052 | 0.13 | 0.08 | 0.72 |
| F × E Waterville 2015 | | | | | | | | |
| NDF | 147 | 83.95 | 1.89 | 82.06 | 1.894 | 0.77 | 2.15 | 0.77 |
| ADF | 147 | 55.85 | 1.77 | 52.30 | 3.550 | 0.64 | 3.72 | 0.84 |
| ADL | 147 | 10.37 | 0.63 | 6.71 | 3.657 | 0.41 | 3.69 | 0.91 |
| CELL | 147 | 45.48 | 1.32 | 45.21 | 0.274 | 0.64 | 0.90 | 0.76 |
| HEMI | 147 | 28.16 | 1.01 | 29.41 | −1.246 | 0.38 | 1.48 | 0.84 |
| C | 145 | 46.08 | 7.29 | 46.10 | −0.015 | 0.03 | 7.47 | −1.37 |
| N | 147 | 0.145 | 0.057 | 0.151 | −0.006 | <0.01 | 0.07 | −0.05 |
| F × E Mansfield 2015 | | | | | | | | |
| NDF | 170 | 80.04 | 1.87 | 76.30 | 3.741 | 0.54 | 4.04 | 0.62 |
| ADF | 170 | 50.60 | 1.76 | 46.94 | 3.655 | 0.58 | 3.89 | 0.66 |
| ADL | 170 | 8.30 | 0.75 | 5.61 | 2.686 | 0.32 | 2.76 | 0.86 |
| CELL | 170 | 42.28 | 1.25 | 41.58 | 0.701 | 0.55 | 1.25 | 0.60 |
| HEMI | 170 | 29.32 | 0.72 | 28.59 | 0.730 | 0.25 | 1.00 | 0.55 |
| C | 132 | 42.77 | 1.64 | 43.67 | −0.906 | 0.03 | 1.94 | 0.32 |
| N | 153 | 0.381 | 0.169 | 0.214 | 0.166 | 0.14 | 0.23 | 1.22 |
| F × E Pullman 2017 | | | | | | | | |
| NDF | 342 | 81.66 | 3.21 | 80.93 | 0.725 | 0.75 | 1.77 | 1.08 |
| ADF | 342 | 53.99 | 2.73 | 53.27 | 0.723 | 0.69 | 1.69 | 1.10 |
| ADL | 342 | 7.02 | 0.84 | 7.09 | −0.064 | 0.24 | 0.74 | 0.83 |
| CELL | 342 | 46.97 | 2.29 | 46.46 | 0.514 | 0.79 | 1.17 | 1.06 |
| HEMI | 342 | 27.66 | 1.65 | 27.42 | 0.245 | 0.43 | 1.27 | 0.96 |
| C | 336 | 45.41 | 0.42 | 43.12 | 2.292 | 0.17 | 2.39 | 0.24 |
| N | 341 | 0.233 | 0.081 | 0.173 | 0.059 | 0.42 | 0.09 | 0.73 |
| F × E Mansfield 2017 | | | | | | | | |
| NDF | 343 | 75.96 | 3.97 | 74.62 | 1.345 | 0.33 | 3.53 | 0.91 |
| ADF | 343 | 47.31 | 3.63 | 45.92 | 1.393 | 0.40 | 3.14 | 0.96 |
| ADL | 343 | 5.96 | 1.00 | 5.70 | 0.256 | 0.14 | 0.98 | 0.64 |
| CELL | 343 | 41.35 | 2.93 | 40.33 | 1.029 | 0.44 | 2.43 | 0.99 |
| HEMI | 343 | 28.65 | 1.81 | 28.49 | 0.159 | 0.10 | 1.74 | 0.67 |
| C | 336 | 45.31 | 0.51 | 42.60 | 2.705 | 0.00 | 2.96 | 0.001 |
| N | 345 | 1.005 | 5.824 | 0.124 | 0.881 | 0.06 | 5.87 | 28.32 |

NDF is neutral detergent fiber, ADF is acid detergent fiber, ADL is acid detergent lignin, CELL is cellulose, HEMI is hemicellulose, C is carbon, N is nitrogen. n is number of samples in calibration set; SD is standard deviation; Bias is the difference between the mean of reference data and the mean of NIRS predicted values; $R^2_{pred}$ is coefficient of determination; SEP is standard error of prediction.

**Table 5.** NIRS Coefficients of Pearson Correlation (and *P* values) of laboratory reference data and NIRS predicted values for NDF, ADF, ADL, cellulose, hemicellulose, C, and N in five environments from the Finch × Eltan breeding population.

| **F × E Pullman 2015** | | | | | | | |
|---|---|---|---|---|---|---|---|
| Trait | NDF | ADF | ADL | Cellulose | Hemicell | Carbon | Nitrogen |
| Correlation | 0.73 | 0.75 | 0.72 | 0.71 | 0.71 | 0.54 | 0.36 |
| *p* value | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| **F × E Waterville 2015** | | | | | | | |
| Trait | NDF | ADF | ADL | Cellulose | Hemicell | Carbon | Nitrogen |
| Correlation | 0.88 | 0.80 | 0.64 | 0.80 | 0.61 | −0.17 | −0.03 |
| *p* value | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | 0.04 | 0.73 |
| **F × E Mansfield 2015** | | | | | | | |
| Trait | NDF | ADF | ADL | Cellulose | Hemicell | Carbon | Nitrogen |
| Correlation | 0.73 | 0.76 | 0.57 | 0.74 | 0.50 | 0.17 | 0.38 |
| *p* value | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | 0.05 | <0.001 |
| **F × E Pullman 2017** | | | | | | | |
| Trait | NDF | ADF | ADL | Cellulose | Hemicell | Carbon | Nitrogen |
| Correlation | 0.87 | 0.83 | 0.49 | 0.89 | 0.66 | 0.41 | 0.65 |
| *p* value | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| **F × E Mansfield 2017** | | | | | | | |
| Trait | NDF | ADF | ADL | Cellulose | Hemicell | Carbon | Nitrogen |
| Correlation | 0.57 | 0.63 | 0.37 | 0.66 | 0.32 | <0.01 | 0.24 |
| *p* value | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | 0.94 | <0.001 |

NDF is neutral detergent fiber, ADF is acid detergent fiber, ADL is acid detergent lignin, CELL is cellulose, HEMI is hemicellulose, C is carbon, N is nitrogen. $\alpha = 0.05$ for the probability level.

In order to derive accurate predictions, the spectral data of a validation population must be relatively similar to the spectra of the calibration population. As a general rule, spectra with a Mahalanobis distance above 3.0 are considered outliers and may be difficult for an equation to predict [41]. The very low prediction accuracy of the Finch × Eltan population in Mansfield 2017 for all traits ($R^2_{pred}$ range = 0.00–0.44) was surprising due to similarities between the spectral data of this population and the population used for the calibration equation. Approximately 85% of the spectra from Mansfield 2017 samples had Mahalanobis distances below 3.0 when compared with the calibration set. The Mansfield 2017 location did have some variability across the field in early spring growth due to snowdrifts that laid in the field, resulting in some lines being under snow cover for a longer period, and could have affected the straw composition. The SEP was quite high for most traits, indicating that there may be a lack of agreement between spectral information and the reference method [39]. However, it is still possible to get accurate predictions for samples that have a Mahalanobis distance above 3.0 [41]. The spectral data from Waterville 2015 was quite dissimilar to that of the calibration population but was predicted with the best accuracy for NDF (Table 4). Every spectra from samples within this environment had a Mahalanobis distance above 3.0. Nevertheless, to improve the predictive ability and increase the reliability of our models on breeding populations, it is likely that the number of environments included in the calibration will need to be increased.

## 4. Conclusions

The predictive ability of a NIRS equation is more reliable and accurate when a broad and robust range of data is used in the calibration. Our broad NIRS models were successful in predicting NDF, ADF, and cellulose of the first validation set with high accuracy whereas hemicellulose and ADL were predicted with lower accuracy. The overall predictive ability of NIRS decreased when used to predict the same traits in the Finch × Eltan breeding population but was still moderately high

for NDF, ADF, and cellulose and suitable for our purposes of estimating decomposition potential. The C and N prediction accuracies were too low across every environment to be trusted. Using NIRS for screening, rather than prediction, will identify whether a sample fits into a range of high or low NDF, ADF, and cellulose values, which will be sufficient for recommendations and breeding purposes. Grouping NDF, ADF, and cellulose values into a "high" or "low" category, accompanied with C and N values obtained through TruSpec analysis, will provide an estimate of fast or slow decomposition for individual cultivars. Additional samples from a wider range of environments would be beneficial for increasing the predictive accuracy and reliability of the NIRS models and would ultimately assist the transition to conservation farming.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4395/9/8/462/s1, Table S1: Summary statistics for neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL), cellulose (CELL), hemicellulose (HEMI), carbon (C), and nitrogen (N) in Pullman 2016, Central Ferry 2017, Pullman 2017, and Mansfield 2017, Table S2: Near-infrared spectroscopy (NIRS) calibration statistics of the specific equations developed from the population of 480 in individual environments. Traits include neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL), cellulose (CELL), hemicellulose (HEMI), carbon (C), and nitrogen (N). Table includes trait, math treatment, number of samples (*n*), mean, standard deviation (SD), standard error of calibration (SEC), coefficient of determination ($R^2$), standard error of cross-validation (SECV), 1 minus the variance ratio (1-VR), standard deviation to standard error of cross-validation ratio (SD/SECV), Table S3. Near-infrared spectroscopy (NIRS) validation statistics displaying laboratory reference measurements vs. NIRS predicted results of the specific equations developed from the population of 480 in individual environments. Measurements for neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL), cellulose (CELL), hemicellulose (HEMI), C, and N. Includes trait, number of samples (*n*), range of reference data, lab mean, lab standard deviation (Lab SD), NIRS predicted mean, bias, coefficient of determination ($R^2$), standard error of prediction (SEP), and slope.

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