Near infrared spectroscopy for characterisation of plant litter quality

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Summary

We investigated the ability of Near Infrared Reflectance Spectroscopy (NIRS) for the rapid determination of several chemical properties of plant litters. The chemical properties included fractions that potentially affect decomposition dynamics in peatlands: total carbon, total nitrogen, extractable (soluble) substances, holocellulose (sum of cellulose and hemicelluloses), sulphuric acid insoluble lignin (Klason lignin), CuO oxidation products of lignin: vanillin (V1), vanillic acid (V2), acetovanillone (V3), 4-hydroxybenzaldehyde (P1), 4hydroxyacetophenone (P2), 4-hydroxybenzoic acid (P3) and ferulic acid (C2), as well as C:N and N:lignin ratio. Samples included litters of 9 plant species, representing 5 groups of plant litter: graminoid, deciduous foliage, conifer foliage, wood and moss. Relationships were found between the chemical properties and NIR spectra using partial least squares (PLS) regression. The predictive power of NIR spectroscopy varied for the different litter properties as well as the datasets. Using both the combined and the branch data sets, very good NIR calibrations were obtained for total carbon and nitrogen, ash content, nonpolar (dichlormethane) extractives, ethanol extractives and total extractives (sum of all soluble substances), holocellulose, C:N, and N:lignin ratio, with r^2 that from 0.80 to 0.99. Using only the combined dataset very good calibrations were also obtained for acetone extractives, water extractives, lignin, P2, P3, C2, V1, V2 and V3, with r^2 from 0.81 to 0.97. NIRS proved to be an accurate and fast method for the determination of plant litter quality in peatlands.

Key index words: decomposition, litter quality, NIRS, peatlands

Introduction

Litter decomposition is one of the key processes in ecosystem functioning and its rate is regulated by the combination of several factors. The quality of plant litter is one of the most important ones (Laiho, 2006) and initial litter quality has been used as a decay predictor in many studies (e.g. Meentemeyer, 1978; Berg and Staaf, 1980; Taylor *et al.*, 1989). Yet, the conventional chemical analyses involved in characterisation of litter quality are costly, time consuming and therefore unlikely to be used routinely for the large sample sets used in complex ecological studies. Near infrared reflectance spectroscopy (NIRS, 780-2500 nm) is an established analytical technique which offers the potential for the accurate, quick and inexpensive characterisation of various organic materials. NIRS has been mainly applied in agricultural science, e.g. assessing forage quality (Norris *et al.*, 1976; Garnsworthy, 2000). In ecological studies, NIRS has been successfully used for the determination of organic compounds in soils (e.g. Dalal and Henry, 1986; Coûteaux *et al.*, 2003), peat (Beining, 2001), or to characterise the composition of forest foliage and forest litters (Wessman *et al.*, 1988; Joffre *et al.*, 1992). NIRS has also been used as a direct decay predictor, litter decomposability was actually predicted more accurately by NIRS than by the initial litter composition measured by standard chemical methods (Gillon *et al.*, 1999b).

The aim of this study was to test the ability of NIRS to characterise the chemical composition of a variety of plant litters typical of different peatland sites, by developing NIR-calibrations for N and several C fractions potentially affecting decomposition dynamics in peatlands.

Materials and methods

Litter materials

Litters of 9 plant species, representing 5 types of peatland plant litter: graminoid, deciduous foliage, conifer foliage, wood and moss, were air dried at room temperature to about 6-8% moisture content and analyzed for their chemical composition. The analyses were selected to divide the litter into organic chemical fractions that are supposed to behave differently during decomposition (Berg and Matzner, 1997) as the further interest of our research group will focus on predicting decomposition rates of these litters. These fractions were extractable (soluble) substances, holocellulose (sum of cellulose and hemicelluloses), sulphuric acid insoluble lignin (Klason lignin), and CuO oxidation

products of lignin: vanillin (V1), vanillic acid (V2), aceto-vanillone (V3), 4-hydroxybenzaldehyde (P1), 4-hydroxy-acetophenone (P2), 4-hydroxybenzoic acid (P3) and ferulic acid (C2). More information about the methods used can be found in Vávøová *et al.* (2008).

Spectral measurements

NIR spectra were obtained with a FieldSpec Pro FR spectroradiometer (ASDI Colorado). Dried and milled samples were presented to the instrument on a Petri dish. Spectra consisting of 20 averaged scans were collected at 5 different sections of the dish and averaged for each sample. Each spectrum consisted of reflectance measurements between 350 and 2500 nm, i.e. reflectance in both visible and Near-IR part was measured. The 350-400 nm part of the spectra was removed as it contained a lot of noise. Reflectance (R) was transformed to absorbance (A) using A = log (1/R).

Multivariate data analyses

Data analyses were performed by partial least squares (PLS) regression (Esbensen, 2002; Martens and Naes, 1991) using The Unscrambler, version 9.2, software package (Camo Process AS; Oslo, Norway). As spectral data pre-processing strongly influences the prediction performance of calibration models (e.g. Gillon *et al.*, 2004), we investigated a number of preprocessing options: smoothing by moving average and Savitzky-Golay smoothing (Savitzky and Golay, 1964), transformation by first and second derivative, standard normal variate (SNV), detrending (DT) (Barnes *et al.*, 1989) and SNV-DT combined with Savitzky-Golay

smoothing (Fig.1). Models were built on the transformed data (1) for the entire spectrum measured in both the visible (400-780 nm) and the NIR region (780-2500) and (2) for the NIR region only (7802500 nm). For each quality parameter, we compared (1) the model calibrated for various litter types (combined dataset,) and (2) model calibrated for pine branch litters only (branch dataset). The prediction abilities of the models were tested using full cross-validation (Martens and Naes, 1991). Therefore, the predictions are independent as they are based on regression models that do not include the predicted data. The r^2 values, root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP, in this study calculated as the root mean square error of cross-validation), and the ratio of the Y-variable standard deviation to RMSEP (RPD) were used for estimating the accuracy of the models (Vavrova *et al.*, 2008).

Results and discussion

Models based only on the NIR part (780 – 2500nm) of the spectra performed better in predicting litter quality parameters, compared to the models using the entire spectrum in both visible and NIR part (400 - 2500 nm). This is inconsistent with earlier studies where the visible region also provided useful predictive information for litter properties, mass loss, and foliage moisture content, and predictions were more accurate when the full spectrum was taken into account rather than just the NIR or visible region (Gillon *et al.*, 1993; Gillon *et al.*, 2004). Our samples were visually examined prior to the collection of NIR spectra. A range of
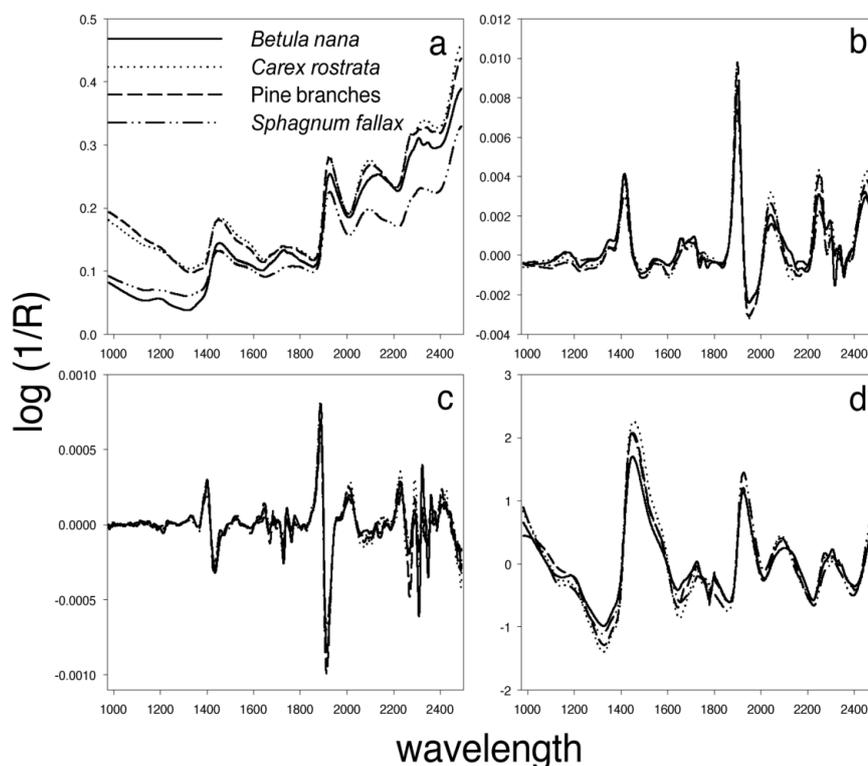

Figure 1. NIR spectra of litter samples of *Betula nana, Carex rostrata, Pinus sylvestris* and *Sphagnum fallax* without transformation (a), transformed by 1st derivative (b), 2nd derivative (c) and SNV-DT (d).
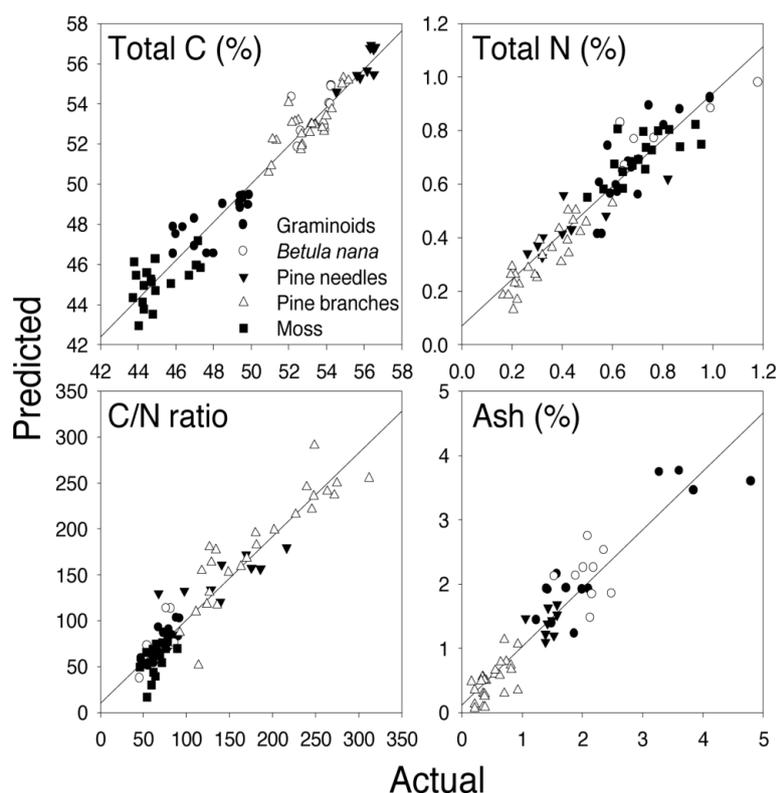
Figure 2. Predicted vs. actual values for litter chemical parameters of the combined dataset

colours was evident between and within different litter types. We assume that excluding the visible region prevents the masking of information within the NIR region. NIR spectra transformed by the second derivative combined with Savitzky-Golay smoothing showed the best performance in predicting most of the quality parameters. There is no best spectral pre-treatment that could be generally used for predicting properties of all types of samples, as the optimal pre-treatment method is very instrument and sample-presentation dependent. Usually, trial and error is the only way to optimise the spectral pre-treatment by searching the lowest prediction error (Chodak *et al.*, 2002; Coûteaux *et al.*, 2003). The predictive power of NIR spectroscopy varied for the different litter properties as well as the datasets. Using both the combined and the branch data sets, very good NIR calibrations were possible for total carbon and nitrogen, ash content, nonpolar (dichlormethane) extractives, ethanol extractives and total extractives (sum of all soluble substances), holocellulose, C:N, and N:lignin ratio (Fig. 2) based on r^2 that varied from 0.80 to 0.99. Using only the combined dataset very good calibrations were also possible for acetone extractives, water extractives, lignin, P2, P3, C2, V1, V2 and V3, with r^2 from 0.81 to 0.97. The models combining all the different litter types performed better than the models constructed for the pine branch litter only, based on r^2 and RPD, the ratio of the Y-variable standard deviation to the root mean square error of prediction (RMSEP). However, RMSEP was generally smaller when a branch litter property was predicted by the branch model compared to the prediction using the combined model, indicating the potential of improving the NIR calibrations by constructing specific models for different groups of litter.

Acknowledgements

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