

EU LIFE Programme project "Demonstration of climate change mitigation potential of nutrients rich organic soils in Baltic States and Finland"

REPORT

ON IMPLEMENTATION OF THE PROJECT

DEMONSTRATION OF CLIMATE CHANGE MITIGATION MEASURES IN NUTRIENTS RICH DRAINED ORGANIC SOILS IN BALTIC STATES AND FINLAND

WORK PACKAGE

TOOLS FOR MODELLING OF IMPACT OF CLIMATE CHANGE ON GHG EMISSIONS (C.2)

ACTIONS

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SUMMARY

Traditional methods available for studying nutrient concentrations and other soil properties involve several steps, are rather time-consuming, involve hazardous chemicals, and may result easily to systematic differences in the outcome. Infrared spectroscopy is a rapid, cost-effective and relatively easy-to-use technique that has long been used for characterization of different sample materials. Infrared spectroscopy is based on each chemical bond absorbing infrared radiation, where mid-infrared ranges have been used to enhance or replace conventional soil analyses. The main soil components absorbing infrared radiation in organic soils are carbohydrates, aromatics, acids, and aliphatics. Infrared spectra can either be used for direct interpretation of the chemical composition, or for creating calibration models. Calibration models are regression models based on a calibration data set that consists of samples with known composition plus their infrared spectra. These models may then be used to predict the composition of unknown samples based on their infrared spectra only. Building representative standardized spectral libraries has been put forward is a priority task for spectral studies. Current spectral libraries mostly include data from mineral soil samples and are thus not readily applicable for organic soils.

The aim of this study was to start building a spectral library for organic soils (including peat) and to create initial calibration models to evaluate method potential to predict pH value and C, N, P, K, Ca, Mg and humic acid concentration in peat samples. For soil parameter prediction model calibration and validation soil samples from peatlands with various land-uses, as well as samples from naturally wet and drained forest stands with different forest site type classification were selected. Sample set dominated by organic soils with some exceptions of mineral soil from deeper soil layers.

In the scope of this study it was observed that RSD value considerably lower than 2 signals a possible difficulty to apply current methodological approach for quantitative analyte prediction in unknown samples. The highest potential of prediction performance was observed for pH, Ca and Mg, but the lowest perspective for P and K. C, N and humic acid as well as other parameter prediction performance may be improved by primary increasing count and variety of calibration samples (spectra) and secondary by increasing count of measurement replicates for the same sample to discard replicates that increases relative standard deviation of prediction replicates above threshold, e.g. 10%. It was observed that mostly the highest performance of analyte prediction in peat samples was for prediction models elaborated by peat soil calibration data set only, addition of forest soil sample spectra to calibration data set did not improve model performance. Nevertheless, also for such calibration data sets with peat soils only, PCA often indicated significant spectral differences that could have added uncertainty to values predicted by model. In the scope of the study separation of spectra by PCA did not improve model quality as model robustness may have decreased to insufficient number of spectra. Higher number of spectra would allow to make separate calibration models by focusing more on PCA results. Afterwards these models could be applied to unknown samples by guidance of values of spectral residues and Mahalanobis distance to match appropriate models and unknown spectra. Other potential solution for improving model prediction capabilities may be improvements of sample preparation procedure, e.g., ensuring more homogenous samples.



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1. INTRODUCTION

Information on soil nutrient concentrations and other soil properties, e.g., characteristics of the soil organic matter are needed for many purposes. The rates of many soil processes and, consequently, soil greenhouse gas emissions depend at least to some extent on the nutrient regime of the site (IPCC 2014). Accordingly, nutrient concentrations of organic soils are routinely measured in several laboratories. Several methods are traditionally available, the most common ones traditionally including wet digestion or dry ashing of samples and analysis of mineral nutrient concentrations with Inductively Coupled Plasma Spectroscopy or Atomic Absorption Spectrophotometer. The work involves several steps, is rather time-consuming, and measurements done at different times with slightly different procedures may lead to systematic differences between different batches (Laiho et al. 2008). Also, these methods usually involve use of strong acids with its hazards. Nitrogen concentrations need further to be analyzed with a different method than the other main nutrients. Thus, there is space for a new harmonized method for such analyses.

Infrared spectroscopy is a rapid, cost-effective and relatively easy-to-use technique that has long been used for characterization of different sample materials, including determination of several chemical and biological characteristics of soils (e.g., Confalonieri et al. 2001; Terhoeven-Urselmans et al. 2008; Cécillon et al. 2009; Bellon-Maurel and McBratney 2011). Infrared radiation is the region of electromagnetic radiation where wavelengths range from ca. 780 nm to ca. 1 mm. Infrared waves are thus longer than those of visible light. Infrared spectroscopy is based on each chemical bond absorbing infrared radiation in a specific manner that depends on the nature of the bond. Thus, an infrared absorbance spectrum, showing for each wave-length or wave-number the proportion of radiation absorbed by the sample, shows the relative abundance of different chemical bonds in the sample, that is, a summary of the chemical composition of the sample (e.g., Coates 2000).

The main soil components which absorb infrared radiation in organic soils are carbohydrates, aromatics, acids, and aliphatics. While the peak heights formed in IR spectrum alone are not directly quantitative, after area normalization and baseline correction, comparing peak heights between samples is useful for determining the relative abundance of major structural groups (e.g., exemplifying graph adapted from Hodgkins et al. 2018, below). The relative abundances of carbohydrates and aromatics are very well suited for evaluating origin of soil materials and levels of humification or decomposition in organic soils. Carbohydrates (O-alkyl-C) are primarily found in peat-forming plants as cellulose, and are the more labile constituent of peat (LaRowe and Van Cappellen, 2011; Tfaily et al. 2014; Hemingway et al. 2019). O-alkyl-C abundances have been shown to be the best proxy for decomposition potential compared to other factors such as soil pH, depth (age), and element ratios such as C/N, O/C, and H/C (Baldock et al. 1997; Leifeld et al. 2012).





The infrared range is usually divided into three regions: near infrared (nearest the visible spectrum), mid infrared, and far infrared. Both near infrared (NIR) and mid infrared (MIR) ranges have been used to enhance or replace conventional soil analyses. MIR has often been found somewhat superior to NIR in soil analyses (e.g., McCarty et al. 2006; Viscarra Rossel et al. 2006; Vohland et al. 2014), even though the benefits of each technique may depend on the context or the variables being studied (Madari et al. 2006; Ludwig et al. 2008; Reeves 2012; Straková et al. 2020).

Infrared spectra can either be used for direct interpretation of the chemical composition based on the absorbance intensities at different wave lengths (e.g., Coates 2000), or for creating calibration models (e.g., Munawar et al. 2020), or both (e.g., Straková et al. 2020). Calibration models are regression models based on a calibration data set that consists of samples with known composition plus their infrared spectra. These models may then be used to predict the composition of unknown samples based on their infrared spectra only. Multiple soil properties can be estimated for each sample from a single spectrum. Nutrient concentrations in soils can be estimated only using calibration models, and such models have been successfully built (e.g., Confalonieri et al. 2001; Viscarra Rossel et al. 2006; Du et al. 2009), also for wetland soils (Cohen et al. 2005).

Single studies with specific sample sets may yield results that are not replicable, and the models built on a limited range of samples cannot generally be applied on samples outside that range. Consequently, building representative standardized spectral libraries has been put forward is a priority task for spectral studies (e.g., Cécillon et al. 2009; Nocita et al. 2015; Straková et al. 2020). Using the USDA NSSC-KSSL spectral library and development of appropriate statistical models, it has recently been shown that reasonably accurate and precise estimates of a range of soil properties can be obtained (Comstock et al. 2019; Dangal et al. 2019; Ng et al. 2019; Nocita et al. 2015; Sanderman et al. 2020; Seybold et al., 2019; Shepherd and Walsh 2007, Shepherd et al. 2015; Terhoeven-Urselmans et al. 2010; Viscarra Rossel et al. 2008; Wijewardane et al. 2018). Yet, extreme sample diversity in a library may also lead to poor modeling outcomes (Reeves et al. 2009). Current spectral libraries mostly include data from mineral soil samples and are thus not readily applicable for organic soils.

The aim of this study was to start building a spectral library for organic soils (including peat) and to create initial calibration models to evaluate method potential to predict pH value and C, N, P, K, Ca and Mg concentration in peat samples.



2. METHOD DESCRIPTION

2.1 Principle

In the scope of this study mid-Infrared (MIR) Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS) is applied. DRIFTS is a IR spectroscopy technique that allows rapid measurements to dried, homogenized sample without additional sample preparation procedure. During measurements a samples of <2 mm air-dry soil are placed in the wells of a microplate, inserted into a microplate reader for MIR data collection. The infrared light on a sample is reflected and transmitted at different amounts depending on the bulk properties of the material. The resulting MIR spectra are stored for future analysis. Because of the small diameter of microplate wells at 6-mm, the homogeneity and particle-size of the sample are important to examine when the spectral results are interpreted (Baldock and Hawke, 2010). The main purpose of collecting MIR spectra is to estimate soil properties from spectra from models built on spectral and measured data.

2.2 Spectral and measured data model building

In the scope of this study chemometric model building was based on multivariate calibration analysis. Multivariate calibration make use of not only a single spectral point but take into account spectral features over a wide range. Purpose of this calibration technique is to correlate measured absorption of infrared radiation with properties of analyzed peat and soil samples. To determine concentration of more than one analyte in each sample simultaneously partial least square (PLS) fit method is used - the information contained in the spectra of the calibration samples are compared to information of the concentration values using a PLS regression. PLS algorithm deployed ensures that relevant principal components (factors) of spectral data matrix are used for calibration to find the best correlation function between spectral and concentration data. Ultimately calibration function calculated by Bruker software QUANT is the model used for then analysis of unknown samples later. To test model reliability model validation procedure was performed.

The error of calibrations depends on not only the quality of the MIR spectra, but also on the accuracy of the measured data to which spectra are modeled. Even for a property that lends itself to being modeled, poor quality measured data will result in high model errors.

Model performance on unknown samples will depend on how well the soil variability was captured in the calibration. For optimal model performance and because of the great variability of soils, it is therefore important to capture the variability of the specific soils in the target area to which the calibration is intended to apply.



2.3 FTIR spectrometer specification

| Parameter | Description |
|----------------------|--|
| Instrument type | INVENIO-S. |
| Accessory | HTS – XT equipped with MCT type medium band detector with |
| | working range 12000600 cm ⁻¹ , 8 h Dewar hold time. Samples |
| | are entered in microplate format sample carriers plate with 24 |
| | sample cups. |
| Optics Configuration | Right Exit with: MIR, KBr, LN MCT Mid, Microplate reader. |
| Spectral range | at least 7500350 cm ⁻¹ . |
| Signal-to-noise | at least 55 000 (1 min measurement time, @4 cm ⁻¹ resolution, |
| | peak-to-peak). |
| Spectral resolution | adjustable in range 0.4128 cm ⁻¹ . |
| Wavenumber | <0.0005 cm ⁻¹ @15001600 cm ⁻¹ . |
| precision | |
| Wavenumber | > 0.01 cm ⁻¹ @15001600 cm ⁻¹ . |
| accuracy | |
| Photometric accuracy | <0.1% transmission. |
| Software | OPUS 8.5(SP1) Build: 8, 7, 10 / DB: 8,7,10,139 |
| | Software includes a functionality of creating and managing PLS |
| | based quantitative calibrations, including functionality of PCA |
| | (principle component analysis) and automatic finding of correct |
| | spectral regions for each quantified parameter. |



2.4 Instrument method settings

| Category | Parameter | Value |
|---------------|--------------------------------|-----------------------------------|
| Scan settings | Resolution | 4 cm-1 |
| | Sample Scan time | 64 scans |
| | Background scan time | 64 scans |
| | Data range | 4000 to 600 cm ⁻¹ |
| | Result spectrum | Absorbance |
| | Saved data blocks | Absorbance, single chanel; sample |
| | | interferogram, background, |
| | | background interferogram |
| | Additional tratment | Disabled |
| | Atmospheric compensation | Disabled |
| Optic | External synchronization | Off |
| | Source setting | MIR |
| | Beamsplitter | KBr |
| | Optical filter setting | Open |
| | Aperture setting | 6 mm |
| | Acessory | HTS-XT LN-MCT Mid |
| | Measurement channel | Right Exit |
| | Background measurement | Right Exit |
| | channel | |
| | Detector setting | LN MCT Mid (microplate reader) |
| | Scanner velocity | 15 kHz |
| | Sample signal gain | Automatic (pream. gain A) |
| | Background signal gain | Automatic (pream. gain A) |
| | Delay after device change | 0 |
| | Delay before measurement | 0 |
| | Optical Bench Ready | Off |
| Acquisition | Wanted high frequency limit | 8000 |
| | Wanted low frequency limit | 0 |
| | High pass filter | On |
| | Low pass filter | Automatic |
| | Acquisition Mode | Double Sided, Forward-Backward |
| | Correlation mode | Off |
| | External analog signals | Off |
| FT | Phase resolution | 32 |
| | Phase Correction mode | Power Spectrum |
| | Aphodization function | Blackman-Harris 3-Term |
| | Zerofilling factor | 2 |
| | Perform interferogram non- | Enabled |
| | linearity correstion before FT | |



2.5 <u>Sample testing procedure</u>

Before sample processing it is ensured that instrument is warmed-up After cooling HTS-XT detector with liquid nitrogen for 30 minutes, instrument performance qualification according to manufacturer's instructions is conducted.

Air dried samples sieved through 2 mm sieve and milled till fine powder are filled in sample cups of sample carrier plate in 3 replicates. Therefore, for each sample three subsamples are scanned. Samples in each sample cup are compressed by matching diameter steel rod. Samples are handled with care to avoid sample cross contamination within sample wells. Sample carrier plate and sample cups before handling next samples are cleaned mechanically by using a brush.

As the optical bench is not purged, background scan is performed for each sample plate prior to scanning of samples to compensate for fluctuating concentrations of atmospheric gases.

Spectral interferograms are processed by Fourier transform to convert them to absorbance spectra which are then saved as a new Bruker opus file for each sample.



2.6 Spectral data processing and calibration model building

Samples studied

For purpose of this study 3 sample sets generally consisting of organic soil sampled in Latvia were selected from soil archive of LSFRI "Silava". Reference values of soil parameters were acquired in Laboratory of forest environment of LSFRI "Silava" by applying standard methods for all parameters except for humic acid content where national testing method was applied. Although samples were sampled from mostly areas with organic soils also some mineral soil samples were included in sample sets as soils were sampled in depth up to 150 cm. Mineral soil samples were not excluded to check impact of such samples to MIR-DRIFTS prediction model robustness and performance.

Selected 3 sample sets can be distinguished by its origin form drained and naturally wet forest stands with different stand type classification and peatlands with various land-uses:

• Peatlands - soil samples from peatlands with different land-use. Each land-use is represented by 3-4 plots:



- peat extraction site;
- o partially extracted peatland, poorly developed vegetation;
- o partially extracted peatland, covered by bushes and herbaceous plants;
- perennial grassland (pasture);
- o cropland (cereals and sown grasses);
- o cropland (legumes);
- o plantations of blackberries;
- o plantations of cranberries;
- o at least 20 years old pine or spruce stands;
- o at least 20 years old birch stands;
- o natural raised bog;
- o natural transitional bog.



• Forests with drained and naturally wet nutrient-rich organic soil – soil samples from 26 forest site types classified as drained (*Myrtillosa turf.mel.* and *Oxalidosa turf. Mel.*) and naturally wet (*Dryopterioso–caricosa and Filipendulosa*) forest sites with nutrient rich organic soils according to Latvia's national forest site type classification (Bušs, 1981).



• Forests with mineral and organic soils - O horizon from forest stands with naturally dry mineral soil (*Oxalidosa, Hylocomiosa*), drained mineral soil (*Myrtillosa mel.*) and naturally wet organic soil (*Dryopterioso-caricosa*) with reference values of humic acid content.



Description of samples and reference methods

In the scope of this study in total 1891 samples were scanned in 3 replicates by MIR-DRIFTS, 5673 soil spectra are acquired, respectively. Scanned sample set is created by combining 3 sample subsets:

| Sample origin | Reference values | Soil layer | Sample |
|--------------------------|--|------------------------|--------|
| | values available | | count |
| Peatlands | pH _{KCl} ; C _{tot} ; N _{tot} ; HNO ₃ | O horizon, 0 to 50 cm | 794 |
| | extractable P, K, Ca Mg | by 10 cm step, 50-100, | |
| | _ | 100-150 | |
| Forests with drained and | Bulk density, pH_{KCl} ; | O horizon, 0 to 50 cm | 803 |
| naturally wet nutrient | Ctot; Ntot; HNO ₃ | by 10 cm step, 50-75, | |
| rich organic soil | extractable P, K, Ca Mg | 75-100. | |
| Forests with mineral and | Humci acid | O horizon | 100 |
| organic soils | | | |

All samples were tested by conventional methods in the LSFRI "Silava" Laboratory of forest environment:

| Parameter | Instrument | Sample pretreatment | Standard method |
|---------------------|----------------------|------------------------|------------------|
| рНксі | pH meter | Oven dried | LVS ISO |
| - | | | 10390:2002 |
| | | | L/NAC:2005 L |
| C _{tot} | Elementar EL Cube | Mineral soil sieved | LVS ISO |
| | | through 2 mm sieve, | 10694:2006 |
| N _{tot} | | organic soil milled | LVS ISO |
| | | till fine powder | 13878:1998 |
| HNO3 extractable K | Thermo Fisher | Microwave digestion | LVS EN ISO 11885 |
| HNO3 extractable Ca | Scientific iCAP 7200 | | |
| HNO3 extractable Mg | Duo | | |
| HNO3 extractable P | | | |
| Humic acid | F-TS 1000 Titroline | Air dried | (Pāvule, 1978) |
| | 5000 | | |

2.7 Model elaboration and validation

Each of sample subsets by sample origin and relevant spectra were divided in 2 separate data sets (all spectra replicates of one soil sample destined in only one data set):

- 70% of sample spectra for calibration model elaboration;
- 30% of sample spectra for model verification.

Acquired data subsets were combined by spectrum use - for calibration or verification. Combined calibration spectra set were used for calibration model elaboration. For each of parameter several calibration models (calibrations) were created for further evaluation. Each of calibration versions for one soil parameter is outcome of different combinations of main model elaboration decisions:

• outlier spectrum exclusion from calibration. Identification and assessment of spectrum outliers using visual representation of model version characteristics acquired by model cross-validation provided by OPUS software. Spectrum outliers were identified by:



 spectrum Mahalanobis distance value¹;

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40 35 30 25 20 15 10 5 0 -5 -10 0 6 8 10 14 18 22 26 30 34 38 2 4 Rank: 10 R² = 88.62 RMSECV = 3.41 Bias: 0.0231 RPD: 2.96 Validation No 1 + Ntot_OrgSoil_20210628_1.q2

Prediction vs True / Ntot dry [g/kg] / Cross Validation

 plotting value predicted by model vs. reference value;

- plotting predicted value of spectrum replicate vs. mean of predicted values;

Prediction vs True / Ntot dry [g/kg] / Cross Validation



Deviation to Mean vs Sample Number / Ntot dry [g/kg] / Cross Validation



¹ The Mahalanobis distance serves to quantify outliers. During the PLS calculation the Mahalanobis distances of each calibration spectrum is determined. From these values the threshold of the Mahalanobis distance is derived. Spectra of unknown samples can be reliably analyzed using a calibration function if their Mahalanobis distance is within this threshold.



 plotting difference between bias of predicted value vs. reference value;

Difference vs True / Ntot dry [g/kg] / Cross Validation









Validation No 1 Ntot_OrgSoil_20210628_1.q2

Score 3 vs Score 1 / Ntot dry [g/kg] / Cross Validation



Validation No 1 Ntot_OrgSoil_20210628_1.q2

• Selection of spectrum preprocessing method:

results of PCA (Principal

component analysis)

0

- o no spectral data preprocessing (No);
- constant offset elimination (COE);
- straight line subtraction (SLS) : fits a straight line to the spectrum and subtracts it. This accounts for a tilt in the recorded spectrum;

² The result of a factorization never describes completely the variance of the spectral data matrix and the concentration data matrix. The remaining part which is not accounted for by the factorization is called the residual. The spectral residual is important for the recognition of outliers. The bigger the residual, the more likely is the samples an outlier.



- vector normalization (VN) normalizes a spectrum by first calculating the average intensity value and subsequent subtraction of this value from the spectrum. Then the sum of the squared intensities is calculated, and the spectrum is divided by the square root of this sum;
- min-max normalization (MMN): first subtracts a linear offset and then sets the y-maximum to a value of 2 by multiplication with a constant. Used similar to the vector normalization;
- multiplicative scattering correction (MSC) performs a linear transformation of each spectrum for it to best match the mean spectrum of the whole set. This method is often used for spectra measured in diffuse reflection;
- o internal standard (IS);
- first derivative (FD) calculates the first derivative of the spectrum. This method emphasizes steep edges of a peak. It is used to emphasize pronounced, but small features over a broad background. Spectral noise is also enhanced;
- o second derivative (SD) : similar to the first derivative, but with a more drastic result;
- first derivative + straight line subtraction (FD+SLS);
- first derivative + vector normalization (FD+VN);
- first derivative + multiple scattering correction (FD+MSC).
- Selection of calibration regions in spectra:
 - Manually;
 - Automatic by OPUS software, options;
- General A frequency region is divided into 10 equal subregions. To find the optimum combination
 the calculation starts with 10 subregions and successively excludes one subregion. This procedure
 continues until the mean prediction error value does not improve further;
- General B frequency region is divided into 10 equal subregions. To find the optimum combination
 the calculation starts with one subregion. After the best subregion has been found a second subregion
 is added. After the best combination of two subregions has been found a third subregion is added and
 so on. The best combination of subregions is searched by adding and leaving out further subregions
- Count of ranks³ used in calibration by evaluating:
 - o calibration root mean square error of cross-validation depending of count of ranks
 - o correlation between predicted value of model and reference value depending of count of ranks.

During elaboration of different calibration model versions, each of version were evaluated by crossvalidation – the same spectral data set is used for both model calibration and validation. During crossvalidation multiple cycles of calibration and validation are performed as data set used for validation must not be part of the calibration set. During every cycle small fraction of spectral data set is excluded from calibration and used for validation. During next cycle previous validation data set is returned to calibration data set and another fraction of calibration data is transferred to validation data set. Cycles are repeated until all samples have been used for validation. Count of spectral data samples used for validation were chosen as proposed by Opus software. Cross-validation results are used for initial evaluation of calibration model performance only. Quality of elaborated model versions were compared by:

- R² coefficient of determination;
- RMSECV root means square error of cross validation;
- RPD residual prediction deviation;
- rank calibration factors used by model.

Final evaluation of calibration model versions are done by external test validation In order to choose the most reliable version from all calibration model versions elaborated, an external test set validation was

The rank is number of PLS vectors. The quality of the chemometric model depends on the choice of the correct number of factors needed; this is also called the rank of the model. Choosing a too small rank results in underfitting so that not all features can be explained by the model. On the other hand, including too many factors (rank too high) leads to overfitting and only adds noise, in fact degrades the model.



performed by verification data set that was not used in calibration model elaboration to compare model performance analyte concentration prediction characteristics were compared:

- RMSEP root mean square error of prediction;
- bias systematic deviation of the measured (predicted) values from the true value due to a particular measurement method, for example. In our case, it is the difference between the average true value and the average measured value of the validation set samples;
- SEP standard error of prediction (bias-corrected) is a quantitative measure for the preciseness of a test set validation. It indicates the standard deviation of all bias-corrected measured values from the true value
- RPD residual prediction deviation is the ratio of standard deviation to standard error of prediction
- offset the y-value of the regression line if x = 0
- slope a value of the regression line.

One model or combination of models (separate model models for defined concentration range prediction) with the best performance by root mean square error of prediction and slope value were used for prediction method combined uncertainty evaluation. Combined uncertainty was calculated using calibration model data (true and predicted values of the analyte) according to NordTest methodology (Magnusson et al. 2012). Estimated combined uncertainty includes measurement result repeatability (standard error of measurement replicate results), bias from true value (nominal analyte concentration in sample) and reference method uncertainty. Combined uncertainty calculations steps:

1. Calculation of repeatability standard deviation of a predicted values (calculated form analyte concentration prediction from sample spectra scanned in 3 repetitions, each scan made for different subsample of the sample):

$$S_r = \frac{\sum S_i}{n}$$
 [%], where:

- Sr Repeatability standard deviation of a predicted values;
- S_i relative standard deviation of 3 prediction replicates;
- n sample count.
- 2. Calculation of uncertainty component for bias:

$$RMS_{bias} = \sqrt{\frac{\Sigma(bias_i)^2}{n}}$$
 [%], where

*RMS*_{bias} – root mean square of bias;

 $bias_i$ – difference between predicted concentration and true (measured by reference method) analyte concentration in an individual sample;

n – sample count.

$$u(bias) = \sqrt{RMS_{bias}^2 + u(Cref)^2} [\%], \text{ where:}$$

u(bias) – uncertainty component for bias; u(Cref) – combined uncertainty of reference method.

3. Calculation of combined uncertainty:

$$u_c = \sqrt{S_r^2 + (u(bias))^2}$$
[%], where

4. Calculation of expanded uncertainty:

$$U = 2 * u_c [\%]$$
, where

U – Expanded combined uncertainty (close to 95 % confidence interval)



3. RESULTS

3.1 <u>pH</u>

During pH prediction model elaboration 7 calibration model versions $(pH_v1 - pH_v7)$ were created by using different combinations of all available soil spectra (peat and forest soil sample spectra separately as well as combined). All elaborated pH prediction models were validated by two datasets: all available peat sample spectra and combination of both peat and forest soils sample spectra. Performance of elaborated pH prediction models were comparable for prediction of pH in both peatland and combined peatland and forest land validation sample test set. Higher RMESP for prediction of pH for combined peatland and forestland validations sample set can be explained that also pH range for this data set is wider. Although PCA indicated spectral feature differences in peat and forest soils sample spectra, it was observed that soil matrix has low impact on pH prediction model performance (**Kļūda! Nav atrasts atsauces avots.**).



Validation No 2 + P_pH_OrgSoil_20210621_1.q2

Figure 1. PCA results indicating soils matrix effect on differences of spectra features. (Sample type is indicated by color: green – peat; brown – forest soil with Ctot >200 g kg-1, gray – forest soil Ctot<200 g kg-1)

Validation results (RMSEP and slope) indicates that pH_v3 is the most appropriate calibration model version to predict pH value in both beat and forest soil samples. According to prediction model results, RMSEP of pH prediction in peat (pH range 2.0 – 6.6) and forest soil (pH range 1.9-7.6) samples is 0.172 and 0.287 accordingly (Table 1). Most appropriate spectra preprocessing method was multiplicative scattering correction.

Table 1. Relationship between average predicted humic acid value and relative standard deviation of replicates

| Validation dataset | Model version | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|-----------------------|---------------|---------|-------|----------|-------|------|--------|-------|
| Peatlands, | pH_v3 | 711 | 0.172 | 0.0142 | 0.172 | 6.28 | -0.055 | 1.012 |
| pH 2.0-6.6 | pH_v7 | 711 | 0.176 | 0.0133 | 0.175 | 6.15 | -0.057 | 1.013 |
| | pH_v6 | 711 | 0.179 | 0.0296 | 0.176 | 6.11 | -0.042 | 1.004 |
| Peatlands + | pH_v7 | 1392 | 0.286 | -0.00118 | 0.286 | 4.52 | 0.092 | 0.978 |
| forest lands, | pH_v1 | 1392 | 0.287 | 0.00527 | 0.287 | 4.51 | 0.116 | 0.971 |
| pH 1.9-7.6 | pH_v3 | 1392 | 0.287 | -0.00016 | 0.287 | 4.51 | 0.045 | 0.989 |



pH values predicted in peat samples by model version pH_v3 has high correlation (0.99) with reference pH values (Figure 2), in addition, predicted and references value linear regression slope is irrelevant (1.012). Predicted value bias from reference value is evenly distributed across pH value range of available validation soil sample set (Figure 3).



Prediction vs True / pH [units] / P_pH_OrgSoil_20210621_3.q2

Figure 2. Linear regression of pH reference (x axis) and predicted values (y axis)



Differ vs True / pH [units] / P_pH_OrgSoil_20210621_3.q2

Figure 3. Relationship between reference (x axis) and bias of predicted (y axis) pH values

Results of calibration model version pH_v3 validation shows that at most cases bias of predicted pH value in peat samples does not exceed \pm 10 % (RMS bias 5.5 %) (Figure 4), while average relative standard deviation of pH prediction by peat 3 sub-sample replicates is 1.5 % (Figure 5). According to reference method uncertainty and acquired pH value prediction bias and repeatability characteristics, combined peat pH prediction uncertainty is 6.2 % (Table 2).





Figure 4. Relationship between predicted pH value and relative bias from reference value



Figure 5. Relationship between average predicted pH value and relative standard deviation of replicates

| Table 2. | pН | prediction | method | validation | summary | |
|----------|----|------------|--------|------------|---------|--|
| | | | | | | |

| Concentration range | RMS _{bias} , % | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, | Expanded combined |
|---------------------|----------------------------|---------------|---------------|-----------|--------------------------|-------------------|
| | | | | | % | uncertainty, % |
| рН 2.0 — 6.6 | 5.51 | 2.36 | 6.00 | 1.47 | 6.18 | 12.35 |



3.2 Total carbon (C)

As a result of total carbon prediction calibration 25 different model versions ($Ctot_v1 - Ctot_v25$) were elaborated by using peatland and forest land samples separately as well as both calibration at sets combined. None of elaborated models could provide consistent C content prediction in whole calibrated concentration range (33.7 - 540.0 g C kg-1), therefore 2 separate and most appropriate model versions were chosen for 2 calibration ranges. Concentration threshold of 540 g kg-1 were determined by evaluating visual representation of model validation results – plots of predicted value bias vs reference value and predicted value vs reference value. Model version validation results show that model ($Ctot_v5$) with the best performance for C prediction covering concentration range above 540 g C kg-1 the best performance was for model ($Ctot_v1.2$) calibrated by peat and forest land soils with high C content combined. Such observation may point out that there were not enough peat soil samples in calibration data set to build robust C prediction model for high concentration range by using peat samples only. Also, RPD value was significantly higher for model versions calibrated and validated by peat and forest soils data sets combined pointing out that C prediction in peat samples model performance may be improved by increased number calibration samples with higher diversity of peatland samples (Table 3).

| Validation dataset | Model | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|--|-----------|---------|-------|---------|------|------|---------|-------|
| | version | • | | | | | | • |
| Peatlands, | Ctot_v5 | 714 | 36.3 | -4.17 | 36.1 | 2.6 | 87.803 | 0.839 |
| 33.7-699.0 g C kg ⁻¹ | Ctot_v8 | 714 | 36.8 | -2.36 | 36.7 | 2.55 | 88.114 | 0.835 |
| | Ctot_v9 | 714 | 37.2 | -0.597 | 37.2 | 2.52 | 94.899 | 0.818 |
| Dootlondo | Ctot_v5 | 381 | 42.4 | -20.3 | 37.3 | 2.6 | 58.394 | 0.918 |
| Pedudius, 22.7 E40.0 g C kg ⁻¹ | Ctot_v9 | 381 | 42.9 | -18.6 | 38.7 | 2.5 | 61.759 | 0.907 |
| 55.7-540.0 g C Kg | Ctot_v8 | 381 | 43.5 | -19.5 | 39 | 2.49 | 52.159 | 0.93 |
| Dootlondo | Ctot_v8 | 333 | 27.1 | 17.3 | 20.9 | 1.56 | 37.783 | 0.905 |
| Peatiands, | Ctot_v1.2 | 333 | 27.7 | 17.7 | 21.3 | 1.53 | 0.238 | 0.969 |
| 540.0-699.0 g C kg | Ctot_v5 | 333 | 27.8 | 14.3 | 23.8 | 1.37 | 3.612 | 0.969 |
| Peatlands + forest | Ctot_v2 | 1434 | 41.4 | 0.00413 | 41.4 | 4.22 | 21.895 | 0.951 |
| lands | Ctot_v1 | 1434 | 41.7 | 0.434 | 41.7 | 4.2 | 24.594 | 0.944 |
| 0.8-699.0 g C kg ⁻¹ | Ctot_v3 | 1434 | 41.8 | 0.0298 | 41.9 | 4.18 | 23.693 | 0.947 |
| Peatlands + forest | Ctot_v1 | 354 | 59.6 | -10.1 | 58.8 | 2.56 | 18.065 | 0.956 |
| lands | Ctot_v2 | 354 | 61 | -9.95 | 60.3 | 2.5 | 13.451 | 0.981 |
| 0.8-430.0 g C kg ⁻¹ | Ctot_v3 | 354 | 61.7 | -9.64 | 61.1 | 2.47 | 17.649 | 0.955 |
| Peatlands + forest | Ctot_v1 | 1080 | 26.3 | 1.82 | 26.2 | 1.83 | 129.269 | 0.754 |
| lands | Ctot_v2 | 1080 | 26.9 | 1.88 | 26.9 | 1.78 | 125.381 | 0.761 |
| 430.0-699.0 gC kg ⁻¹ | Ctot_v10 | 1080 | 27.1 | 2.4 | 27 | 1.78 | 139.982 | 0.733 |

| Table 3. | Validation summary | of Ctot | prediction | model | versions | with | lowest | RMSEP |
|----------|--------------------|---------|------------|-------|----------|------|--------|-------|
| | 2 | | 1 | | | | | |

Model version Ctot_v5 was chosen as most reliable for C prediction in peat samples for concentration range bellow 540 g C kg-1 as model verification showed the lowest both RMSEP (42.4) and SEP (37.3) values for this specific model versions, also slope value of linear regression between refference values and predicted value 0.918 is appropriate (Figure 6), as data available for model calibration could not achieve significantly better model performance – for different model versions slope ranged form 0.733 to 0.951. Bias value had no considerable impact on overall performance of elaboratoed model versions as



for most of models versions it ranged from -18.6 to -22.3. Test set validation of model version Ctot_v5 indicated an average bias of -20.3 g C kg-1, however in some sases bias exceeded 100 g C kg-1 (Figure 7). In most cases high bias is observed at C concentration <400 g C kg-1, most likely these samples were taken from deeper peatland layers and had mineral soil admixture. Exclusion of such samples durring model callibration did not iprove C prediction quality in peat samples with concentration range < 540 g C kg-1, therefore it was decided to include them in booth calibration and validation data sets to increase and demonstrate C prediction model robustness.



Figure 6. Linear regression of Ctot reference (x axis) and predicted values (y axis)



Figure 7. Relationship between reference (x axis) and bias of predicted (y axis) Ctot values

For concentration range above 540 g C kg⁻¹ best performance was achieved by model version (Ctot_v1.2) that was calibrated by original peatland and forest soil data sets combined – none of spectras were excluded. That highlights imoprtance of highly diversified sample availability for FTIR-DRIFTS prediction model elaboration with high performance and robustness. Model Ctot_v1.2 validation showed



good slope value (0.969) of regression between predicted and refference values (**Kļūda! Nav atrasts atsauces avots.**). Average bias of predited concentration is 17.7 g C kg⁻¹ (Figure 9) or less then 3% if concentration range is considered.



Figure 8. Linear regression of Ctot reference (x axis) and predicted values (y axis)



Differ vs True / Ctot_dry [g/kg] / OrgSoil_20210603_cal_DS_1.q2

Figure 9. Relationship between reference (x axis) and bias of predicted (y axis) Ctot values

Performance of both chosen models combined is represented in Figure 10 and Figure 11. It can be clearly distinguishable that C prediction quality is decreased when samples with mineral soil admixture are evaluated. C prediction quality is considerable higher if samples with high C content are being tested. If C content is above 400 g kg-1 bias of predicted C values rarelly exceeds 20 % (Figure 10) and relative standard deviation of measurement replicates stays bellow 5 % (Figure 11).





Figure 10. Relationship between predicted C_{tot} value and relative bias from reference value



Figure 11. Relationship between average predicted C_{tot} value and relative standard deviation of replicates.

According to test set validation results, if predicted concentration is bellow 400 g C kg⁻¹ root mean square bias of predicted value is 26 % and relative standard deviation of prediction replicates is 10 %. For concentration range above 400 g C kg⁻¹ estimated bias and repeatability is 6 % and 1 % respectively. If these prediction quality indicators are combined with reference method uncertainty of 2 %, combined uncertainty of C content prediction at concentration range below and above 400 g C kg⁻¹ is 28 % and 6 % respectively.



| Concentration range | RMS _{bias} , % | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, % | Expanded combined uncertainty, % |
|--------------------------|-------------------------|------------|------------|--------|-------------------------------|---|
| < 400 g kg⁻¹ | 26.05 | 1.73 | 26.11 | 10.38 | 28.1 | 56.20 |
| > 400 g kg ⁻¹ | 5.90 | 1.73 | 6.15 | 1.22 | 6.27 | 12.54 |

Table 4. C prediction method validation summary

3.3 <u>Total nitrogen (N)</u>

From 32 calibration model versions created for prediction of N content in peat samples 2 separate versions were found to be most suitable for N prediction in 2 concentration ranges: below and above 13 g C kg-1. At lower range, the best performance was for model version N_v29 for which combination of peatland and forest land sample spectra were combined, althought share of forest soils samples were slightly above 10 % - most of forest soil samples had to excluded from calibration data set to achieve best performance of N prediction in peat samples. While for concertation range above 13 g N kg-1 forest soils sample spectra did not improve quality of model and only peat samples were used in model version N_v15 that performed the best (Table 5). Although model version N_v21 had lower RMSEP, version N_v15 was chose as more apropriate due to higher slope value (0.928).

| Validation | Model | Spectra | | Piec | CED | חחם | Officiat | Slong |
|--|---------|---------|---------|-------------|------|------|----------|-------|
| dataset | version | Spectra | RIVISEP | DIdS | SEP | RPD | Unset | Slope |
| | N_v13 | 627 | 2.61 | 0.187 | 2.61 | 2.88 | 0.988 | 0.909 |
| Peatlands, 4.4-37.4 g kg⁻¹ | N_v4 | 627 | 2.66 | - 0.0352 | 2.66 | 2.82 | 1.408 | 0.894 |
| | N_v18 | 627 | 2.66 | - 0.0352 | 2.66 | 2.82 | 1.408 | 0.894 |
| Poatlands | N_v29 | 411 | 1.46 | -0.398 | 1.41 | 1.62 | 2.182 | 0.793 |
| Pedulatius, $4.4.12.0 \text{ g kg}^{-1}$ | N_v31 | 411 | 1.48 | -0.402 | 1.43 | 1.6 | 2.157 | 0.797 |
| 4.4-13.0 g Kg | N_v27 | 411 | 1.49 | -0.41 | 1.44 | 1.59 | 1.93 | 0.824 |
| Dootlondo | N_v21 | 216 | 3.15 | -0.864 | 3.04 | 2.35 | 5.976 | 0.758 |
| Pedulanus, 12.0.27.4 α k α^{-1} | N_v15 | 216 | 3.17 | 0.909 | 3.04 | 2.35 | 0.611 | 0.928 |
| 15.0-57.4 g kg | N_v19 | 216 | 3.19 | 0.175 | 3.19 | 2.24 | 3.021 | 0.849 |
| Peatlands + forest | N_v13 | 1248 | 3.08 | 0.203 | 3.08 | 2.93 | 1.167 | 0.92 |
| lands, | N_v8 | 1248 | 3.11 | 0.105 | 3.11 | 2.9 | 1.823 | 0.887 |
| 2.6-37.4 g kg⁻¹ | N_v9 | 1248 | 3.14 | 0.0975 | 3.14 | 2.88 | 1.639 | 0.898 |
| Peatlands + forest | N_v27 | 519 | 1.97 | -0.33 | 1.95 | 1.39 | 2.327 | 0.758 |
| lands, | N_v29 | 519 | 2 | -0.405 | 1.97 | 1.38 | 2.548 | 0.74 |
| 2.6-13.0 g kg ⁻¹ | N_v31 | 519 | 2.04 | -0.472 | 1.99 | 1.36 | 2.773 | 0.721 |
| Peatlands + forest | N_v14 | 729 | 3.22 | 0.49 | 3.19 | 1.96 | 2.166 | 0.886 |
| lands, | N_v8 | 729 | 3.34 | 0.703 | 3.26 | 1.91 | 2.856 | 0.848 |
| 13.0-37.4 g kg ⁻¹ | N_v9 | 729 | 3.37 | 0.595 | 3.32 | 1.88 | 3.112 | 0.841 |

Table 5. Validation summary of Ntot prediction model versions with lowest RMSEP

Although there is a good correlation (0.81) between predicted and reference N values at lower concentration range (<13 g N kg-1), it can be distinguished that dispersion of predicted values slightly



increases at concentration range between 7 to 13 g N kg-1. While at concentrations region bellow 7 g N kg-1 dispersion is reduced, observed slope (0.79) of regression between predicted and refference N values introduces considerable N content underestimation (Figure 12). At this concentration region at most cases average bias does not exceed -2.2 g N kg-1 (Figure 13). Attemts to introduce additional calibration at this skewed concentration range could not improve N prediction quality.



Figure 12. Linear regression of Ntot reference (x axis) and predicted values (y axis)



Figure 13. Relationship between reference (x axis) and bias of predicted (y axis) Ntot values

N prediction quality at concentration region above 13 g N kg-1 is considerably higher. Correlation between predicted and reference values oefficient is 0.91 and slope is introduces considerably lower bias to the predicted value (Figure 14). At validated concentration region between 13 and 40 g N kg-1 bias of predicted value rarely exceed 5 g N kg-1 (Figure 15).



Prediction vs True / Ntot_dry [g/kg] / Ntot_OrgSoil_20210628_15.q2



Figure 14. Linear regression of Ntot reference (x axis) and predicted values (y axis)



Figure 15. Relationship between reference (x axis) and bias of predicted (y axis) Ntot values

If both model validation results are combined threshold significant changes of N prediction in peat samples is around 15 g N kg-1 (Figure 16). If predicted N concentration is bellow 15 g kg-1 at most cases bias is limited to 40 %, at higher concentrations bias is reduced significantly RMSbias 15 % and rerely exceeds 20%. At most cases replicate measurement predicted value relative standard error is well bellow 10 % in whole validated concentration region (Figure 17), that can be considered as appropriate performance of environmental sample testing.





Figure 16. Relationship between predicted Ntot value and relative bias from reference value



Figure 17. Relationship between average predicted Ntot value and relative standard deviation of replicates

Estimated relative standard deviation of measurement replicates is around 5 % in the whole calibrated and validated N prediction concentration region from 4.4 to 13.0 g kg-1. According to method validation results root mean squeare bias of predicted value bellow and above concentration 15 g N kg-1, is 19 % and 14 % accordingly. By combining prediction method bias repeatability and reference method uncertainty, combined uncertainty of N concentration prediction in peat samples is 40 % and 32 % at concentration ranges bellow and above 15 g N kg-1 respectively (Table 6).



| Concentration range | RMS _{bias} ,, % | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, % | Expanded combined uncertainty, % |
|-------------------------|--------------------------|------------|------------|--------|-------------------------------|---|
| < 15 g kg ⁻¹ | 19.2 | 13.4 | 19.45 | 5.1 | 20.1 | 40.3 |
| > 15 g kg ⁻¹ | 14.4 | 13.4 | 14.8 | 5.3 | 15.8 | 31.5 |

Table 6. N prediction method validation summary

3.4 Phosphorous (P)

In the scope of this study P calibration attempts encountered considerable difficulties to acquire linear relationship between predicted and reference P concentration value during model calibration procedure (cross-validation). 44 different model versions were created and 2 calibration concentration ranges identified – below and above 0.6 g P kg-1. Validation results of model versions inicate that model version P_v27 is the most suitable for lower concentration range, however acquired slope (0.64) and RPD (1.63) indicates model weaknesses to predict P concentration in peat samples. For higher range acquired RPD value (1.28) of the most suitable model version P_v1 is even lower.

| Validation dataset | Model version | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|--|---------------|---------|--------|----------|--------|------|--------|-------|
| Peatlands | P_v5 | 618 | 0.233 | -0.0124 | 0.233 | 1.62 | 0.134 | 0.637 |
| 0.1-2.2 g kg ⁻¹ | P_v13 | 618 | 0.239 | 0.0142 | 0.239 | 1.58 | 0.137 | 0.551 |
| | P_v7 | 618 | 0.242 | -0.00017 | 0.242 | 1.56 | 0.145 | 0.57 |
| Deatlands | P_v27 | 546 | 0.0828 | -0.00693 | 0.0826 | 1.63 | 0.087 | 0.637 |
| Peatianus, 0.1.0.6 $\alpha k \alpha^{-1}$ | P_v44 | 546 | 0.0902 | -0.0243 | 0.0869 | 1.55 | 0.108 | 0.618 |
| 0.1-0.0 g kg | P_v12 | 546 | 0.0919 | -0.0155 | 0.0907 | 1.49 | 0.089 | 0.668 |
| Deetlende | P_v36 | 75 | 0.399 | 0.116 | 0.384 | 1.29 | 0.531 | 0.45 |
| Peatiands, | P_v1 | 75 | 0.406 | 0.125 | 0.389 | 1.28 | 0.042 | 0.858 |
| 0.0-2.2 g kg | P_v5 | 75 | 0.497 | 0.275 | 0.416 | 1.19 | 0.489 | 0.35 |
| Peatlands + | P_v1 | 342 | 0.708 | 0.252 | 0.663 | 1.37 | 0.565 | 0.406 |
| forest lands | P_v36 | 342 | 0.809 | 0.229 | 0.777 | 1.17 | 0.826 | 0.233 |
| 0.1-0.6 g kg ⁻¹ | P_v5 | 342 | 0.874 | 0.334 | 0.809 | 1.12 | 0.799 | 0.176 |
| Peatlands + | P_v5 | 315 | 0.388 | 0.138 | 0.363 | 1.14 | 0.495 | 0.451 |
| forest lands, | P_v1 | 315 | 0.395 | 0.107 | 0.381 | 1.08 | 0.274 | 0.67 |
| 0.6-2.2 g kg ⁻¹ | P_v7 | 315 | 0.409 | 0.144 | 0.383 | 1.07 | 0.683 | 0.283 |

Table 7. Validation summary of P prediction model versions with lowest RMSEP

Lack of linearity between predicted and reference P concentration values introduces P concentration underestimation at concentration range bellow 0.2 g kg-1 and overestimation at concentration range from 0.2 to 0.6 g kg-1 (Figure 18). Excercise of applying slope and offset values to correct predicted P concentration did not improve root mean square of predicted values. Model version P_v27 at most cases underestimated or overestimated P concentration by ± 18 g P kg-1 (Figure 19).



Prediction vs True / P_dry [g/kg] / P_dry_OrgSoil_20210615_27.q2



Figure 18. Linear regression of P reference (x axis) and predicted values (y axis)



Figure 19. Relationship between reference (x axis) and bias of predicted (y axis) P values

Weak prediction of P concentration higher than 0.6 g kg-1 could be indroduced due to unsufficient callibration samples. Low RPD is linked to lack of clear bias tendency distribution (Figure 20). Validation results of model version P_v1 indicates that at concentration range from 0.6 to 2.2 g P kg-1 bias of predicted value rarely exceeds ± 0.7 g P kg-1 (Figure 21).



Prediction vs True / P_dry [g/kg] / P_dry_OrgSoil_20210615_1.q2



Figure 20. Linear regression of P reference (x axis) and predicted values (y axis)



Figure 21. Relationship between reference (x axis) and bias of predicted (y axis) P values

Bias of predicted P concentration values in peat samples by selected model versions expressed in relative unit shows that at low concentration ranges in some cases bias exceeded 100 % (Figure 22). Such significantly biased prediction values could be introduced by random errors of spectra measurements due insufficient sample homogeneity. This study shows that quality of sample preparation in case of other analytes allowed to acquire RSD of prediction replicates well below 10 %, however for high number of samples P prediction replicate RSD was as high as 20 % and for some samples repeatability was significantly lower than that (Figure 23). In this study 3 sample measurement replicates for same sample were made, higher count of spectra replicates would allow do discard bad spectra and acquire lower RSD and consequently lower also bias values improving overall uncertainty of P prediction model.





Predicted P, g kg⁻¹

Figure 22. Relationship between predicted P value and relative bias from reference value



Figure 23. Relationship between average predicted P value and relative standard deviation of replicates

According to validation of model versions P_v27 and P_v1 results, average relative standard deviation and root mean square bias of prediction values are 9 % and 33 % at concentration range from 0.1 to 0.6 g P kg-1 and 13 % and 28 % at concentration range from 0.6 to 2.2 g kg-1 respectively. Accordingly estimated combined uncertainty of P prediction in peat samples is 74 % at lower concentration range and 67 % at higher concentration range (Table 8).



| Concentration range | RMS _{bias} , | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, % | Expanded combined uncertainty, % |
|--------------------------|-----------------------|------------|------------|--------|-------------------------------|---|
| < 0.6 g kg ⁻¹ | 33.11 | 13.40 | 35.71 | 9.33 | 36.91 | 73.83 |
| > 0.6 g kg ⁻¹ | 27.87 | 13.40 | 30.93 | 13.01 | 33.55 | 67.10 |

| Table | 8 | Р | prediction | method | validation | summary |
|-------|----|---|------------|--------|------------|---------|
| raute | ο. | 1 | prediction | memou | vanuation | Summary |

3.5 <u>Calcium (Ca)</u>

From 33 Ca prediction model versions the most appropriate for peat samples are found to be versions Ca_v29 and Ca_v16 for concentration ranges from 0.3 to 10.0 g Ca kg-1 and from 10.0 to 47,0 g Ca kg-1 accordingly. Model version validation shows that slope value of regression of predicted and P concentration references values for both model versions is above 0.8 and RPD value above 2.0 (Table 9).

| Validation dataset | Model version | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|--|---------------|---------|-------|--------|------|------|--------|-------|
| Peatlands, | Ca_v18 | 627 | 2,73 | -0,49 | 2,69 | 3,69 | 0,563 | 0,991 |
| 0.3-47.0 g kg ⁻¹ | Ca_v16 | 627 | 2,82 | -0,47 | 2,78 | 3,57 | 0,636 | 0,98 |
| | Ca_v28 | 627 | 3,3 | -0,749 | 3,22 | 3,08 | 1,098 | 0,957 |
| Deatlands | Ca_v29 | 456 | 1,05 | -0,037 | 1,05 | 2,15 | 0,327 | 0,902 |
| Peatianus, 0.2.0.10.0 σ kg ⁻¹ | Ca_v26 | 456 | 1,11 | -0,054 | 1,11 | 2,03 | 0,55 | 0,832 |
| 0.3.0-10.0 g kg | Ca_v28 | 456 | 1,12 | -0,038 | 1,12 | 2,01 | 0,525 | 0,835 |
| Dootlondo | Ca_v16 | 174 | 4,41 | -0,707 | 4,37 | 2,05 | 4,223 | 0,84 |
| Pedulanus, 10.0.47.0 g kg ⁻¹ | Ca_v18 | 174 | 4,61 | -1,05 | 4,51 | 1,99 | 5,125 | 0,815 |
| 10.0-47.0 g kg | Ca_v1 | 174 | 4,98 | -1,29 | 4,83 | 1,86 | 8,564 | 0,669 |
| Peatlands + | Ca_v1 | 1122 | 4,74 | 0,0704 | 4,74 | 2,72 | 1,744 | 0,858 |
| forest lands, | Ca_v15 | 1122 | 4,86 | -0,021 | 4,87 | 2,65 | 1,92 | 0,852 |
| 0.1-54.4 g kg ⁻¹ | Ca_v12 | 1122 | 4,9 | -0,048 | 4,9 | 2,64 | 1,944 | 0,852 |
| Peatlands + | Ca_v13 | 621 | 1,66 | -0,281 | 1,64 | 1,49 | 0,761 | 0,85 |
| forest lands, | Ca_v24 | 621 | 1,71 | -0,305 | 1,68 | 1,46 | 1,107 | 0,75 |
| 0.1-10.0 g kg ⁻¹ | Ca_v11 | 621 | 1,74 | -0,343 | 1,71 | 1,43 | 0,825 | 0,85 |
| Peatlands + | Ca_v23 | 501 | 5,85 | -0,473 | 5,83 | 1,81 | 8,958 | 0,656 |
| forest lands, | Ca_v1 | 501 | 6,03 | 0,913 | 5,96 | 1,77 | 7,324 | 0,666 |
| 10.0-54.4 g kg ⁻¹ | Ca v15 | 501 | 6,2 | 0,931 | 6,13 | 1,72 | 7,298 | 0,666 |

Table 9. Validation summary of Ca prediction model versions with lowest RMSEP

In addition, also high correlation coefficient (0.9) of relationship between predicted and Ca reference values indicates good Ca prediction models capabilities in both calibration ranges (Figure 24 and Figure 26). For lower calibration range prediction bias is evenly distributed across whole concentration range from 0.3 to 10.0 g Ca kg-1, estiumate root means squeare error of prediction is 1.05 g Ca kg-1 (Figure 25). For higher concentration range (from 10.0 to 47.0 g Ca kg-1) bias distribution is ratker skewed. From



around 10 to 20 g kg-1 Ca content tens to be uderestimated, but at concentration above 20 g Ca kg-1 – slightly overestimated (Figure 27).



Figure 24. Linear regression of Ca reference (x axis) and predicted values (y axis)



Figure 25. Relationship between reference (x axis) and bias of predicted (y axis) Ca values



Prediction vs True / Ca_dry [g/kg] / Ca_OrgSoil_20210629_16.q2



Figure 26. Linear regression of Ca reference (x axis) and predicted values (y axis)



Figure 27. Relationship between reference (x axis) and bias of predicted (y axis) Ca values

Ca prediction can be characterized with comparably more reduced repeatability at concentration range approximately bellow 5 to 10 g Ca kg-1 where RSD of prediction replicates reaches 40 %, consequently at this concentration range also bias at some cases reaches 200 %. Therefore similar to case of P prediction, also Ca prediction quality can be increased by creating additional spectra replicates for the same tested sample. At concentration range above 5 g kg-1 Ca prediction quality increases considerably (Figure 28 and Figure 29).





Figure 28. Relationship between predicted Ca value and relative bias from reference value



Figure 29. Relationship between average predicted Ca value and relative standard deviation of replicates

According to validation of model versions P_v26 and P_v16 results, average relative standard deviation and root mean square bias of prediction values are 13 % and 46 % at concentration range from 0.3 to 10.0 g P kg-1and 6 % and 25 % at concentration range from 10.0 to 47.0 g kg-1 respectively. Accordingly estimated combined uncertainty of Ca prediction in peat samples is 49 % at lower concentration range and 28 % at higher concentration range (Table 10).



| Concentration | RMS _{bias} , | U(Cref), % | U(bias), % | RSD, % | Combined | Expanded |
|---------------------------|-----------------------|------------|------------|--------|--------------|--------------|
| range | | | | | uncertainty, | combined |
| | | | | | % | uncertainty, |
| | | | | | | % |
| <10 .0 g kg ⁻¹ | 45.96 | 8.97 | 46.82 | 13.00 | 48.60 | 97.19 |
| > 10.0 g kg ⁻¹ | 25.26 | 8.97 | 26.81 | 6.24 | 27.52 | 55.04 |

3.6 Magnesium (Mg)

By different combinations of exclusion of spectral outliers, preprocessing method, selection of calibration regions and count of ranks, 21 Mg calibration versions were elaborated. In order to find the most appropriate calibration model versions for peat screening, elaborated Mg calibration models were validated by different validation spectrum data set versions. It was found that for peat screening combination of 2 acquired calibration model versions would be most appropriate: version Mg_v18 for high concentration range (Mg > 2.5 g kg-1) and version Mg_v21 for low concentration range < 2.5 g Mg kg 1 (Table 11). Although PCA indicated spectral differences between sample groups of peatlands and forest lands, acquired quality of model version Mg_v3 indicates that also combination of booth data sets can be used for robust Mg prediction model.

| Validation dataset | Model version | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|--|---------------|---------|-------|----------|-------|------|--------|-------|
| Deatlands | Mg_v18 | 648 | 0.365 | -0.0141 | 0.365 | 2.67 | 0.119 | 0.904 |
| Peduanus, $0.1.4.4 \text{ g kg}^{-1}$ | Mg_v3 | 648 | 0.38 | 0.00685 | 0.38 | 2.56 | 0.168 | 0.84 |
| 0.1-4.4 g кg | Mg_v19 | 648 | 0.389 | 0.0152 | 0.389 | 2.5 | 0.186 | 0.816 |
| Developmente | Mg_v20 | 564 | 0.263 | 0.00612 | 0.263 | 2.12 | 0.128 | 0.829 |
| Peatiands, 0.1.2 E $a k a^{-1}$ | Mg_v21 | 564 | 0.265 | -0.00166 | 0.266 | 2.1 | 0.13 | 0.837 |
| 0.1-2.5 g кg | Mg_v19 | 564 | 0.276 | -0.0373 | 0.273 | 2.04 | 0.135 | 0.875 |
| Peatlands + | Mg_v3 | 1128 | 0.536 | -0.012 | 0.536 | 2.16 | 0.308 | 0.798 |
| forest lands, | Mg_v1 | 1128 | 0.622 | -0.0325 | 0.622 | 1.86 | 0.409 | 0.742 |
| 0.1-4.4 g kg ⁻¹ | Mg_v6 | 1128 | 0.663 | 0.141 | 0.648 | 1.78 | 0.091 | 0.842 |
| Peatlands + | Mg_v5 | 885 | 0.362 | 0.0314 | 0.361 | 1.8 | 0.295 | 0.66 |
| forest lands, | Mg_v8 | 885 | 0.363 | 0.038 | 0.361 | 1.79 | 0.296 | 0.653 |
| 0.1-2.4 g kg ⁻¹ | Mg_v3 | 885 | 0.445 | -0.122 | 0.428 | 1.52 | 0.16 | 0.96 |

Table 11, Validation summary of Mg prediction model versions with lowest RMSEP

Both model versions chosen as most applicable provide comparably good Mg prediction capabilities due to high correlation between predicted and reference values of Mg concentration in validation tests set peat samples (Figure 30 and Figure 32). Root mean square error of prediction for low concentration range (0.1-2.5 g kg-1) and whole calibration range (0.1-4.4 g kg-1) according to validation results is 0.265 g kg-1 (Figure 31) and 0.365 g kg-1 accordingly (Figure 33).



Prediction vs True / Mg_dry [g/kg] / Mg_dry_OrgSoil_20210610_21.q2



Figure 30. Linear regression of Mg reference (x axis) and predicted values (y axis)



Prediction vs True / Mg_dry [g/kg] / Mg_dry_OrgSoil_20210610_21.q2

Figure 31. Relationship between reference (x axis) and bias of predicted (y axis) Mg values



Prediction vs True / Mg_dry [g/kg] / Mg_dry_OrgSoil_20210610_18.q2



Figure 32. Linear regression of Mg reference (x axis) and predicted values (y axis)



Figure 33. Relationship between reference (x axis) and bias of predicted (y axis) Mg values

Mg concentration prediction performance by combination of model versions Mg_v18 and Mg_v21 was further evaluated by estimating combined uncertainty of predicted values. According to external validation with peatlands data set, prediction performance considerably decreased if predicted value of Mg concentration is bellow ~ 1.3 g kg-1 (Figure 34) when for some samples bias of predicted values exceeded 100 %. Increased measurement bias is related to reduction of prediction measurement repeatability at low concentration range. At concentration range above 1 g Mg kg-1 RSD is mostly well bellow 10 %, however when concentration exceeds 1 g Mg kg-1 at some cases RSD reaches and exceeds RSD of 20 % (Figure 35).





Predicted Mg, g kg⁻¹

Figure 34. Relationship between predicted Mg value and relative bias from reference value



Figure 35. Relationship between average predicted Mg value and relative standard deviation of replicates

If predicted concentration is bellow 1.3 g Mg kg-1 root mean square bias of predicted value is 55 % and relative standard deviation of prediction replicates is 12 %. For concentration range above 1.3 g Mg kg-1 estimated bias and repeatability is 31 % and 4 % respectively. If these prediction quality indicators are combined with reference method uncertainty of 8 %, combined uncertainty of C content prediction at concentration range below and above 1.3 g C kg-1 is 115 % and 65 % respectively.



| Concentration range | RMS _{bias} , % | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, % | Expanded combined uncertainty, % |
|--------------------------|----------------------------|---------------|---------------|--------|-------------------------------|---|
| < 1.3 g kg ⁻¹ | 55.41 | 7.85 | 55.95 | 12.27 | 57.28 | 114.57 |
| > 1.3 g kg ⁻¹ | 31.42 | 7.85 | 32.38 | 4.16 | 32.65 | 65.29 |

| Table | 12 | Mø | prediction | method | validation | summary |
|--------|-----|------|------------|--------|------------|---------|
| 1 auto | 14. | IVIS | prediction | memou | vanuation | summary |

3.7 Potassium (K)

From 22 calibration model versions created for prediction of K content in peat samples 2 separate versions were found to be most suitable for N prediction in 2 concentration ranges: below and above 1.7 g K kg-1. At lower range, the best performance was for model version K_v14 for which only peatland sample spectra were used as calibration data set to achieve best performance of K prediction in peat samples. While for concertration range above 1.7 g K kg-1 forest soils sample spectra did improve quality of model and combination of peat and forest land sample sepctra were used for creation of model version N_v5 that performed the best (Table 13).

| Validation | Model | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|---------------------------------|---------|---------|-------|--------------|-------|-------|--------|-------|
| dataset | version | | | | •=- | | | 0.000 |
| Peatlands | K_v5 | 654 | 0.83 | 0.0929 | 0.826 | 1.36 | 0.33 | 0.351 |
| (0.005-8.8 | K_v11 | 654 | 0.86 | 0.168 | 0.845 | 1.33 | 0.279 | 0.314 |
| g kg⁻¹) | K_v22 | 654 | 0.864 | 0.213 | 0.838 | 1.34 | 0.229 | 0.322 |
| Postlands | K_v14 | 606 | 0.25 | 0.00332 | 0.25 | 1.62 | 0.121 | 0.68 |
| 0.005-1.7 g | K_v18 | 606 | 0.26 | - 0.00248 | 0.26 | 1.56 | 0.147 | 0.628 |
| ٨g | K_v9 | 606 | 0.262 | 0.058 | 0.256 | 1.59 | 0.142 | 0.485 |
| Peatlands, | K_v5 | 48 | 2.81 | 2.39 | 1.49 | 1.18 | 0.345 | 0.313 |
| 1.7-8.8 g | K_v22 | 48 | 2.99 | 2.61 | 1.47 | 1.2 | 0.353 | 0.258 |
| kg-1 | K_v8 | 48 | 3 | 2.51 | 1.67 | 1.06 | 0.762 | 0.179 |
| Peatlands + | K_v2 | 1146 | 0.772 | 0.115 | 0.764 | 1.28 | 0.339 | 0.307 |
| forest lands | K_v1 | 1146 | 0.783 | 0.126 | 0.774 | 1.26 | 0.337 | 0.293 |
| 0.005-8.8 g kg ⁻¹ | K_v11 | 1146 | 0.79 | 0.0838 | 0.786 | 1.24 | 0.348 | 0.342 |
| Peatlands + | K_v18 | 1095 | 0.422 | -0.137 | 0.399 | 1.14 | 0.219 | 0.83 |
| forest lands | K_v8 | 1095 | 0.422 | -0.12 | 0.405 | 1.12 | 0.21 | 0.813 |
| 0.005-2.2 g kg ⁻¹ | K_v14 | 1095 | 0.356 | -0.107 | 0.34 | 1.34 | 0.223 | 0.76 |
| Peatlands + | K_v5 | 51 | 3.06 | 2.48 | 1.81 | 0.928 | 1.058 | 0.185 |
| forest lands | K_v22 | 51 | 3.24 | 2.54 | 2.04 | 0.821 | 1.312 | 0.115 |
| 2.2-8.8 g kg ⁻¹ | K_v8 | 51 | 3.25 | 2.72 | 1.79 | 0.936 | 1.219 | 0.094 |

Table 13. Validation summary of K prediction model versions with lowest RMSEP



Model version K_v14 was chosen as most appropriate for K prediction in peat samples for concentration range from 0.01 to 1.7 g K kg-1 as model verification showed the lowest both RMSEP (0.25) and SEP (0.25) values for this specific model versions, however slope value of linear regression between refference values and predicted value 0.68 is rather low (Figure 36). Data available for model calibration could not achieve significantly better model performance – for different model versions slope ranged form 0.425 to 0.695. Test set validation of model version K_v15 indicates that In most cases bias of predicted K concentration does not exceed 0.3 g K kg-1 (Figure 37).



Figure 36. Linear regression of K reference (x axis) and predicted values (y axis)



Figure 37. Relationship between reference (x axis) and bias of predicted (y axis) K values

Validation of model version for K prediction in concentration range above 1.7 g K kg-1 was not successful as highest acquired corelation coefficient of relationship between predicted and reference K concentration value in validation peat sample test set was 0.54. In order to improve prediction results validation suggests to apply bias correction 2.39 (Figure 39), however calibration and validation sample count was not



sufficient to consider bias correction.



Offset: 0.345 Slope: 0.313 Corr. Coeff.: 0.5369





Figure 39. Relationship between reference (x axis) and bias of predicted (y axis) K values

Performance of both chosen models combined is represented in Figure 40 and Figure 41. Similarly to cases of P and Ca, also K prediction method validation indicates that model performance could be improved by increasing count of spectra replicates to aim towards reduced relative standard deviation of prediction replicates by discarding faulty spectrum.





Figure 40. Relationship between predicted K value and relative bias from reference value



Figure 41. Relationship between average predicted K value and relative standard deviation of replicates

According to test set validation results, if predicted concentration is below 0.5 g K kg-1 root mean square bias of predicted value is 100 % and relative standard deviation of prediction replicates is 17 %. For concentration range above 0.5 g K kg-1 estimated bias and repeatability is 66 % and 8 % respectively. If these prediction quality indicators are combined with reference method uncertainty of 11 %, combined uncertainty of C content prediction at concentration range below and above 0.5 g C kg-1 is 102 % and 68 % respectively (Table 14).



| Table 14. K prediction method validation summar | ĴУ |
|---|----|
|---|----|

| Concentration range | RMS _{bias} , % | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, % | Expanded combined uncertainty, % |
|--------------------------|-------------------------|------------|------------|--------|-------------------------------|---|
| < 0.5 g kg⁻¹ | 100.02 | 10.66 | 100.58 | 16.75 | 101.97 | 203.93 |
| > 0.5 g kg ⁻¹ | 66.30 | 10.66 | 67.15 | 7.81 | 67.61 | 135.21 |

3.8 Humic acid

For prediction of humic acid content in total 13 calibration model versions were created. According model validation results model version 6 provided the most accurate humic acid prediction results (Table 15.)

| Validation dataset | Model version | Spectra | RMSEP | Bias | SEP | RPD | Offset | Slope |
|---------------------------------|---------------|---------|-------|-------------|------|------|--------|-------|
| Peatlands, | 6 | 90 | 24.5 | 8.26 | 23.1 | 1.24 | 31.138 | 0.299 |
| 20.9-138.6 g | 11 | 90 | 24.5 | 8.94 | 22.9 | 1.25 | 31.53 | 0.28 |
| kg ⁻¹ | 13 | 90 | 24.5 | 8.6 | 23 | 1.24 | 31.371 | 0.289 |
| Destheads | 6 | 78 | 8.82 | 0.0945 | 8.88 | 1.99 | 12.711 | 0.73 |
| 20.0 SE 0 σ | 13 | 78 | 9.11 | 0.577 | 9.15 | 1.93 | 14.723 | 0.677 |
| 20.9-85.0 g kg ⁻¹ | 10 | 78 | 9.13 | - 0.0676 | 9.19 | 1.92 | 17.349 | 0.636 |
| Peatlands, | 4 | 12 | 63.4 | 61.7 | 15.3 | 1.23 | 20.191 | 0.278 |
| 85.0-138.6 g | 6 | 12 | 63.1 | 61.3 | 15.4 | 1.23 | 18.757 | 0.293 |
| kg⁻¹ | 2 | 12 | 65 | 63.2 | 15.7 | 1.2 | 20.355 | 0.263 |

Table 15. Validation summary of humic acid prediction model versions with lowest RMSEP

Model version 6 was the moist suitable version for humic acid content prediction in whole available validation data set concentration range from 20.9 to 138.6 g humic acid kg-1. However 2 calibration ranges are distinguished as prediction power significantly reduced if humic acid concentration in reference samples exceeded 85.0 g kg-1. Most likely such reduction in model performance is observed to to isuficcient calibration samples in high humic acid concentration range. Although validation results indicated low slope value also for concetration range bellow 85 g kg-1, acquired RMSEP value is considerably low (8.82 g kg-1) and RPD value is 2 (Figure 42 and Figure 43) indicating that model can be applied for humic acid concentration prediction in unknown samples.



Prediction vs True / Humic_acid [g/kg] / HumicAcid_OrgSoil_20210706_6.q2



Figure 42. Linear regression of humic acid reference (x axis) and predicted values (y axis)



Figure 43. Linear regression of humic acid reference (x axis) and predicted values (y axis)

Validation results indicate that current model significantly underestimates humic acid content if reference value exceeds 85 g kg-1. Correlation analysis for relationship of predicted and references values of humic acid indicates moderate correlation(Figure 44), furthermore average estimated bias of predicted values is and RMSEP is arount 60 g kg-1 (Figure 45).



Prediction vs True / Humic_acid [g/kg] / HumicAcid_OrgSoil_20210706_6.q2



Figure 44. Linear regression of humic acid reference (x axis) and predicted values (y axis)



Figure 45. Relationship between reference (x axis) and bias of predicted (y axis) humic acid values

Validation bias results expressed in relative values (Figure 46) indicates that bias is in range of ± 60 % and samples with humic acid reference concentration above 85 g kg-1 are uncrestimated by ~60 % (Figure 46).





Figure 46. Relationship between predicted humic acid value and relative bias from reference value

According to estimated relative standard deviation that reaches 20 % (Figure 47), humic acid prediction precision can be slight improved by increasing count of spectra replicates for the same sample, but most likely prediction model performance suffers due to insufficient variety of calibration samples.



Figure 47. Relationship between average predicted humic acid value and relative standard deviation of replicates

By taking into account humic acid prediction model validation results on prediction bias and repeatability as well as reference method uncertainty, combined humic acid prediction uncertainty is 26 % and 52 % at concentration range bellow and above 85 g kg-1 threshold accordingly (Table 16).



| Table 16. Humic acid | l prediction | method | validation | summary |
|----------------------|--------------|--------|------------|---------|
|----------------------|--------------|--------|------------|---------|

| Concentration range | RMS _{bias} , % | U(Cref), % | U(bias), % | RSD, % | Combined uncertainty, % | Expanded combined uncertainty, % |
|------------------------------|----------------------------|------------|------------|--------|-------------------------------|---|
| 24-85 g kg ⁻¹ | 22.52 | 10.0 | 24.64 | 8.32 | 26.00 | 52.01 |
| 85.0-138.6 g kg ⁻ | 50.24 | 10.0 | 51.22 | 8.75 | 51.96 | 103.93 |



4. SUMMARIZED RESULTS

In the scope of this study it was observed that RSD value considerably lower than 2 signals a possible difficulty to apply current methodological approach for quantitative analyte prediction in unknown samples. The highest potential of prediction performance was observed for pH, Ca and Mg, but the lowest perspective for P and K (Table 17). C, N and humic acid as well as other parameter prediction performance may be improved by primary increasing count and variety of calibration samples (spectra) and secondary by increasing count of measurement replicates for the same sample to discard replicates that increases relative standard deviation of prediction replicates above threshold, e.g. 10%. It was observed that mostly the highest performance of analyte prediction in peat samples was for prediction models elaborated by peat soil calibration data set only, addition of forest soil sample spectra to calibration data set did not improve model performance. Nevertheless, also for such calibration data sets with peat soils only, PCA often indicated significant spectral differences that could have added uncertainty to values predicted by model. In the scope of the study separation of spectra by PCA did not improve model quality as model robustness may have decreased to to insufficient number of spectra. Higher number of spectra would allow to make separate calibration models by focusing more on PCA results. Afterwards these models could be applied to unknown samples by guidance of values of spectral residues and Mahalanobis distance to match appropriate models and unknown spectra. Other potential solution for improving model prediction capabilities may be improvements of sample preparation procedure (ensuring more homogenous samples).



Table 17. MIR DRIFTS method validation summary

| Parameter | Validated | Calibration | Spectral | Preprocessing | RPD | Combined |
|-----------|----------------------------------|----------------------|-----------------------|---------------|-------|--------------|
| | concentration | dataset ⁴ | regions | | | uncertainty, |
| | range | | | | | % |
| nЦ | nH 2 0-6 6 | D+E | 3996.2-3315.9; | MSC | 6 28 | 6.2 |
| рп | рп 2.0-0.0 | FTF | 2977.9-1617.3 | IVISC | 0.20 | 0.2 |
| | | | 3997.6-3656.7; | | | |
| | 33.7-540.0 g | D | 3318.7-2997.9; | | 26 | 20.1 |
| C | kg⁻¹ | F | 2639.9-1958.1; | | 2.0 | 20.1 |
| C | | | 1620.1-600.4 | | | |
| | 540.0-699.0 g | | 3997.6-2638.4; | | 1 5 2 | 6.2 |
| | kg⁻¹ | P+F | 229-939.9 | FD+VN | 1.53 | 0.3 |
| | | | 3997.6-3656.7; | | | |
| | | | 3318.7-2977.9; | | 1.60 | 22.4 |
| | 4.4-13.0 g kg ⁻ | Р | 2639.9-1958.1; | VN | 1.62 | 20.1 |
| N | | | 1620.1-1279.3 | | | |
| | 13.0-37.4 g | _ | 3318.7-2638.4: | | | |
| | kg ⁻¹ | Р | 2299-939.9 | FD | 2.35 | 15.8 |
| | | | 2979 3-2299: | | | |
| | 0.1-0.6 g kg ⁻¹ | Р | 1959.6-1618.7 | VN | 1.63 | 36.9 |
| Р | 0.6-2.2 g kg ⁻¹ | | 3658 1-2977 9 | | | |
| | | P+F | 2299-1958.1: | FD+VN | 1.28 | 33.6 |
| | 010 212 8 18 | | 1620,1-600,4 | | 1.20 | 0010 |
| | 0.3.0-10.0 g kg ⁻¹ | Ρ | 3996 2-3655 3 | FD+VN | | |
| | | | 3317 3-2976 A | | | 48.6 |
| | | | 2628 <u>1</u> -1056 7 | | 2.15 | |
| Ca | | | 1618 7-1077 0 | | | |
| Ca | | | 2006 2 2627 | | | |
| | 10.0-47.0 g kg ⁻¹ | Р | 2207 C 1056 7 | | 2.05 | 27 5 |
| | | | 1270 2 020 / | | 2.05 | 27.5 |
| | | | 12/9.5-956.4 | | | |
| | 0.1-2.4 g kg⁻¹ | Р | 2299-1279.3; | MSC | 2.67 | 57.3 |
| | | | 941.3-600.4 | | | |
| ivig | 2444 - 1 - 1 | | 3318.7-2977.9; | MCC | 2.4 | 22.7 |
| | 2.4-4.4 g kg ⁻ | Р | 2639.9-2299; | IVISC | 2.1 | 32.7 |
| | 0.005.4.7 | | 1959.9-1279.3 | | | |
| | 0.005-1.7 g | Р | 3997.6-2977.9; | FD | 1.62 | 102.0 |
| к | kg⁻¹ | | 1959.6-939.9 | | | |
| | 1.7-8.8 g kg ⁻¹ | P+F | 3997.6-3317.3; | FD+VN | 1.18 | 67.6 |
| | | | 1959.6-1618.7 | | | |
| | 20.9-85.0 g | F | 3997.6-3317.3 | MSC | 1.99 | 26.0 |
| Humic | kg⁻¹ | | 2979.3-2297 6 | | | |
| acid | 85.0-138.6 g | F | 1959.6-1617 3 | MSC | 1.23 | 52.0 |
| | kg⁻¹ | • | 1555.0 1017.5 | 14150 | 1.25 | 52.0 |

⁴ P - samples originated from peatlands; F - samples originated from forest lands



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