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Use of near-infrared spectroscopy to assess phosphorus fractions of different plant availability in forest soils

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Abstract

The fractionation of soil P into fractions of different plant availability is a common approach to characterize the P status of forest soils. However, quantification of organic and inorganic P fractions in different extracts is labour-intensive and therefore rarely applied for large sample numbers. Therefore, we examined whether different P fractions can be predicted using near-infrared spectroscopy (NIRS).

We used the Hedley method with increasingly strong extractants to determine P in fractions of different plant availability and measured NIR spectra for soil samples from sites of the German forest soil inventory and from a nature reserve in south-eastern China.

The R^2 of NIRS calibrations to predict P in individual Hedley fractions ranged between 0.08 and 0.85. When these were pooled into labile, moderately labile and stable fractions, R^2 of calibration models was between 0.38 and 0.88. Model prediction quality was higher for organic than for inorganic P fractions and increased with the homogeneity of soil sample sets. Useful models were obtained for samples originating from one soil type in subtropical China, whereas prediction models for sample sets from a range of soil types in Germany were only moderately useful or not useful.

Our results indicate that prediction of Hedley P fractions with NIRS is a promising approach to replace conventional analysis, if models are developed for sets of soil samples with similar physical and chemical properties.

1 Introduction

Phosphorus is limiting plant growth and ecosystem productivity in many parts of the world (e.g. Elser et al., 2007; Vitousek et al., 2010). Unlike nitrogen, the world's P stores for the production of fertilizer are finite and the global peak in phosphorus production is expected to occur around 2030 (Cordell et al., 2009). It is therefore of paramount importance to use P as efficiently as possible in agricultural and forestry production systems. In several parts of Europe and other parts of the world, concerns have been expressed that a substantial proportion of forest stands may suffer from phosphorus-limitations (Fox et al., 2011; Khanna et al., 2007; Lorenz et al., 2003). A number of hypotheses to explain this phenomenon of wide-spread phosphorus limitation have been put forward (Mohren et al., 1986; Paré and Berneir, 1989; Gillespie and Pope, 1991). In long-term development of forest ecosystems following disturbance, phosphorus (in contrast to nitrogen) can only diminish and therefore becomes limiting to biological activity. Consequently, increasing P deficiency is also a natural process of ecosystem retrogression (Wardle, 2009), which seems to be accelerated by anthropogenic activities. The increasing demand for forest biomass, e.g. as a source for renewable energy, might exacerbate the P nutrition problem in many forests (Vanguelova et al., 2010). Therefore, suitable methods for monitoring of the current status and the medium to long-term trends of P nutrition in forest ecosystems are urgently needed.

For forest soils, solely total P contents are often measured. But total P is not a meaningful parameter as it is not very sensitive to environmental or management influences over time and is not indicative of the amount of plant available P in forest soils, where P can occur in many organic and inorganic forms of different availability (Khanna et al., 2007). Especially for forest soils it is important to differentiate between organic and inorganic P forms, since organic P, although not directly available for plant uptake, plays a major role in tree nutrition (Turner et al., 2005; Shen et al., 2011; Rennenberg and Herschbach, 2013). Hence, analytical approaches, such as the Hedley fractionation, have been developed to quantify organic and inorganic P in fractions of different plant availability, and these have been successfully applied to characterize the dynamical nature of P availability in forest ecosystems (e.g. Richter et al., 2006). Though the ecological relevance of chemically derived Hedley fractions have been critically discussed in some cases (Turner et al., 2005) and it is still unclear which fractions are relevant for plant growth (Rennenberg and Herschbach, 2013) particularly in forest soils the application of this sequential extraction method has proven to be useful. Here, in contrast to agricultural soils, the slowly cycling P pool contributes substantially to plant nutrition, whereas labile P pools stay relatively constant, indicating that higher amounts of P from more slowly cycling pools “feed” the labile P pool (Compton and Cole, 1998; Richter et al., 2006). However, the Hedley-fractionation method is very time consuming, labour intensive and therefore costly, which renders it unsuitable for the analysis of large numbers of samples (Cécillon et al., 2009). Therefore, it would be useful, if Hedley-P fractions could be determined by means of an indirect and more inexpensive technique. For this purpose, the use of near-infrared spectroscopy (NIRS) may be a promising approach. NIRS is a rapid and non-destructive analytical method routinely used in a wide range of fields, mostly in quality control in the chemical, forage or food industry. In the field of soil sciences, NIRS has been successfully applied to predict soil chemical and soil biological parameters like C or N contents (Chang et al., 2001; Ludwig et al., 2002; Zornoza et al., 2008). An overview of available reflectance spectra for different soil properties is available at the global soil vis-NIR spectral library (World Agroforestry Centre (ICRAF) and ISRIC-World soil Information, 2010) However, since soil consists of a combination of solid particles of organic and mineral origin, liquids and gas, it represents a difficult material for spectral analysis. Furthermore the mineral fractions of soil, which are commonly the major portion of soils, are usually hardly visible for NIRS (Malley et al., 2004). Despite its complexity and heterogeneity, the spectral information of soils is surprisingly uniform. For example, 30 soil types of to the USDA soil classification system could be grouped into only 5 different spectra classes (Stoner and Baumgardner, 1981). Owing to the low dipole moment between P and oxygen, P or phosphates cannot be excited by infrared radiation and subsequently not detected directly with NIRS. However, P can be detected indirectly, if it is bound organically or through correlation with other soil properties being detectable by NIRS.

To develop reliable NIRS models, it is essential to achieve high quality in spectral data sets. Several publications on NIRS deal with the influence of the quality of soil samples on spectral information. Stenberg et al. (2010) and Brunet et al. (2007) discussed the influence of ground soil samples in comparison with 2 mm sieved samples and found increasing model quality for the more homogeneous ground samples. The quality of the data with regard to the heterogeneity of samples was addressed by Abrams et al. (1987) and Shenk and Westerhaus (1993). Global models used for the prediction of forage quality in hay, where "global" means that the model is based on the largest sample population comprising a wide variety of hay samples and hay composition from many sites, produce as good predictions as local models derived from one single site. However, in other studies using plant material (pine needles), both, improvements and reductions in model quality for more heterogeneous data sets (addressed as global) when compared with homogeneous (local) data, were observed (Gillon et al., 1999). Reductions in model quality were observed for prediction of C content and sample sets with high variation in chemical composition or high spectral variation. Since high variation in chemical composition and spectral properties is true for forest soil samples, it might be a challenging process to build robust models. The problem of detecting soil characteristics using NIRS methods is not new (Stoner and Baumgardner, 1981; Ben-Dor and Banin, 1995; Udelhofer et al., 2003; Cécillon et al., 2009; Genot et al., 2011). To our knowledge, up to now only few publications (Guerrero et al., 2010; Sankey et al., 2008) have addressed the problem of NIRS model calibration and prediction quality depending on the homogeneity respectively heterogeneity of forest soil samples and none of these has focused on soil P.

Currently, there are only few NIRS models available to predict soil-P parameters, e.g., NIRS-prediction models for Mehlich-III extractable P (Chang et al., 2001), for total P and exchangeable P (Malley et al., 2004). Hitherto, there have been no studies focusing on the use of NIRS to predict organic and inorganic Hedley-P fractions in forest soils. This study aimed to examine the general ability of NIR methods to do so. Specifically we addressed the following hypotheses:

1. Hedley fractions of different P availability can be sufficiently well predicted through NIRS.
2. The quality of predictions through NIRS models is higher for organic than for inorganic P fractions.

3. The quality of predictions of P fractions depends on the homogeneity of soil sample data sets.

2 Material and methods

2.1 Soil samples

Two different sets of mineral soil samples were used for this study. Approximately half of the soil samples originated from the German nationwide forest soil inventory (BZE). The BZE data set covers 282 archived soil samples from 145 sites. From each site, if available, two samples (0–5 cm and 10–30 cm depth) were analyzed. Including 70 sites in Baden-Württemberg (70 samples 0–5 cm, 69 samples 10–30 cm), 23 sites in Hessen (23 samples from both depths), 33 sites in Lower Saxony (32 samples 0–5 cm, 28 samples 10–30 cm) and 19 sites in Saxony Anhalt (18 samples 0–5 cm, 19 samples 10–30 cm). BZE samples are composite samples from 8 replicates (BMEL, 2009). The samples included in this data set were selected to cover the majority of forest soil types in Germany and a large variation in total phosphorous concentration. Development of robust NIRS-models requires sample populations that cover the whole calibration range with an approximately even distribution of samples across the range of the variable to be predicted. In contrast, populations with normally distributed samples tend to overestimate low values and underestimate high values in model calibration (Williams, 2001). The BZE soil samples were grouped by their soil type in ten major groups: regosols ($n = 20$), Gleysols ($n = 6$), Luvisols ($n = 59$), Vertisols ($n = 2$), Podzols ($n = 10$), Chernozem ($n = 2$), Stagnosols ($n = 38$), chromic Cambisols ($n = 10$) and Anthrosols ($n = 4$) (IUSS Working Group WRB, 2006). Additional 131 samples belong to the Cambisols and Umbrisols, which are summarized in the German soil classification under the major soil type "Brown Earth". The total P content covered by the BZE samples ranged from 58 to nearly 2800 mg kg^{-1} (Table 1). Owing to the large pedodiversity within this dataset we aimed to select a less heterogeneous sub dataset. Depending on the complexity of samples at least about 100 samples respectively spectra are necessary to perform a successful model development. However, for the BZE samples no clear correlation (data not shown) between total P and individual P fractions or other soil properties such as total C, N and pH (Table 2) could be found to guide such a selection. Only the group BZE Cambisols/Umbrisols was less heterogeneous regarding soil characteristics and included enough samples to provide a suitable subset. As this group is still heterogeneous, we further restricted the group according to the German soil classification to “typical Brown Earth” samples (Table 1). These remaining 84 samples are referred to as “Brown Earths”.

The other half of the soil samples originated from the international Research project “Biodiversity and Ecosystem Functioning in China (BEF China)” (Bruelheide et al., 2011). The 294 soil samples from the BEF China project were collected from 27 so-called Comparative Study Plots (= CSP, 30 m × 30 m) in the Gutianshan National Nature Reserve, which has a size of 81.07 km^2. At all 27 CSPs the soil type was a Cambisol (reference soil group after WRB, 2006) comparable to the “typical Brown Earth” after the German classification. Thus the 294 BEF samples represented a more homogeneous sample set than the BZE samples. At each CSP, nine soil cores that were evenly distributed across each CSP were collected. One bulk sample was then combined from the nine cores, for each of the three depth increments (0–5 cm, 5–10 cm and 10–20 cm), i.e. 81 samples in total. At twelve CSPs, an additional 37 samples were taken from the three topmost diagnostic soil horizons, predominantly Ah and Bw horizons (at one plot, the 4 topmost horizons were sampled) of representative soil profiles of the CSPs. In addition, 176 samples (0–20 cm) were collected in four replicates from 44 so-called Neighbourhood Diversity Tree Clusters which were located in close proximity of some of the permanent Comparative Study Plots. Total P content of all BEF samples ranged from 26 and to 330 $mg\,kg^{-1}$ (Table 1).

Both sample sets, BZE and BEF, contained samples that originated from different depth but the same location (soil cores). Since these samples might not have been spatially independent, the autocorrelation among samples might influence the quality of NIRS models. For example, the validation may not be truly independent, if calibration and validation sample sets contain samples that are systematically correlated with each other. To address this issue, we calculated the Durban–Watson coefficient as a measure of autocorrelation between measured and predicted values and compared this coefficient between sample sets from all soil depth (containing samples from the same location) and from one soil depth only (spatially independent). This test did not indicate autocorrelation within our sample sets. In addition we found no differences for the Durban–Watson coefficient for all BZE samples (depth: 0–5 cm and 10–30 cm) and BZE samples sets from one depth only. Since there was no indication of autocorrelation between samples of different depth, we included all samples in our calibration and validation steps.

The data for C and N content as well as the pH-Values of the BZE samples were provided by the North Western German Research Institute and the Forest Research Institute Baden-Wuerttemberg. Data was measured according to the Handbuch Forstliche Analytik (BMEL, 2009). Total soil carbon and nitrogen contents of the horizon-wise samples and the three depth increments of the BEF samples were determined after dry combustion (1150 °C) with an element analyzer (Elementar Vario EL III) (DIN ISO 10964). Since the material is non calcareous, total soil carbon equals soil organic carbon. For these samples, pH values were derived in H_2O (2.5 : 1water solution to soil) with a Sentix 81 electrode and pH meter (WTW, Germany). C and N contents of the 176 neighbourhood diversity samples of the BEF dataset were determined with a TruSpec Elemental Analyzer (Leco, USA) and pH values were derivedin H_2O (2.5 : 1 water solution to soil) with a blueline electrode and pH meter (Schott, Germany).

All soil samples were dried at 40 °C for 24 h and sieved (2 mm). For C and N analyses samples were finely ground. The intensity of sieving respectively grinding has an impact on the reproducibility and the distribution of extractable P over the fractionation process (Tiessen and Moir, 2008). Due to the more “natural” extractability of P compared to ground samples and the ecological importance of soil aggregates, we used 2 mm sieved soil samples for fractionation.

Before measurement of the NIR spectra, the samples were ground to powder by a mixer mill MM400 (Retsch, Germany) and dried at 40 °C over night again.

2.2 Phosphorus fractionation

For development of near-infrared spectroscopy models, the spectral information needs to be calibrated with values from reference analysis. The commonly used technique for phosphorus fractions in soils is the sequential extraction method according to Hedley (Hedley et al., 1982b). Several authors have discussed the usefulness of this method to determine P in fractions of distinctly different solubility (Cross and Schlesinger, 1995; Condron and Newman, 2011; Yang and Post, 2011).

In the protocol applied to the samples, 0.5 g soil was extracted by different extractants with increasing strength (Fig. 1), starting with distilled water containing an anion exchange resin (Resin), followed by sodium bicarbonate, 0.5 M ($NaHCO_3$), sodium hydroxide, 0.1 M (NaOH), sodium hydroxide, 0.1 M with ultrasonic treatment (S-NaOH), hydrochloric acid, 1 M (1 M HCl) and a final acid digestion (residual). Tiessen and Moir (2008) introduced an additional extraction step with hot concentrated hydrochloric acid (HCl conc.) before the final digestion. Our fractionation scheme considers all of these 7 fractionation steps, but uses 25 mL solution for the extractions and 2.2 mL concentrated nitric acid for the final acid digestion. The whole fractionation process is described in detail by Tiessen and Moir (2008).

Total P content as index value for the sum of all fractions was measured separately with the nitric acid digestion, which is a standard method recommended by the German forest soil survey (BMEL, 2009).

Phosphorous was determined colorimetrically with the molybdenum blue method described by Murphy and Riley (1962) modified by John (1970), but keeping the ammonium molybdenum concentration at $10\,g\,L^{-1}$. Every extract needs to be adjusted for pH, as development and stability of the blue phosphomolybdic complex is pH dependent (Drummond and Maher, 1995; Huang and Zhang, 2008; Tiessen and Moir, 2008) The P extracted within every step is only partly detectable as free phosphate.

To determine the organically bound phosphate, the $NaHCO_3$ –, both NaOH – and the HCl conc. extracts were oxidized with ammonium persulfate in an autoclave and the difference between total P after digestion (TP) and the free phosphate in the extract (Pi) provides the organically bound P(Po) (Rowland and Haygarth, 1997; Tiessen and Moir, 2008). The amount of organically bound P in the Resin and the 1 M HCl extracts were considered negligible (Tiessen and Moir, 2008) and therefore not analysed. We summed up the values for Pi and Po for the two NaOH fractions, because the ultrasonic treated NaOH step is chemically hardly different from the main NaOH fraction and a differentiation between these two fractions with NIRS did not seem meaningful. Similar considerations applied to the distinction between Pi and Po in the HCl conc. extract, since concentrated HCl is a strong oxidant and an additional oxidation with persulfate is chemically comparable. In our observation the precision of the Pi value of the HCl conc. extract is less satisfying than the TP value and this might be an indicator for an incomplete reaction during the boiling procedure. Also several organic phosphates are unstable under these acid conditions (Turner et al., 2005) and the results of Pi and Po of the HCl conc. fraction lacked reproducibility within our standard and replicates. The total P content of the HCl conc. fractions showed good reproducibility and therefore was used for calibration.

In summary, we selected the following fractions to perform calibrations with NIRS: Pi Resin, Pi $NaHCO_3$, Po $NaHCO_3$, Pi NaOH, Po NaOH, Pi 1 M HCl, P HCl conc., P residual. For the purpose of subsequent statistical analyses, the Hedley fractions were grouped by their solubility in labile (Pi Resin, Pi and Po $NaHCO_3$), moderately labile (1 M HCl, Pi and Po NaOH) and stable P pools (P HCl conc. and P residual) as commonly found in literature. (Cross and Schlesinger, 1994; Stevenson and Cole, 1999; De Schrijver et al., 2011; Yang and Post, 2011). Several tests were conducted to ensure that Hedley fractions were reproducible and accurately determined. One indicator of the reliability of the Hedley Fractionation Method is the recovery rate of total P in the sum of fractions, which was very good for the soils in this study (Fig. 2). Only for samples with high P content, the sum of fractions may either systematically exceed the total P content or the amount of measured total P may be underestimated. Errors for samples with high P content could occur either due to necessary dilution steps for measuring fractions with very high P concentration, where small differences during colorimetric measurements lead to relatively high errors for the final value, or to incomplete digestion of P with nitric acid. To avoid these sources of error, we performed repeated measurements of these samples and we reduced the sample weight to 400 mg and increased the amount of acid to 3 mL in these samples. In addition, this problem occurred only in a very low proportion of samples (10 out of 576) and removing these samples from the data set does not change the calculated recovery rate.

2.3 Near-infrared spectroscopy

Molecules with dipole moments can be exited to stretching, bending and rotating oscillations by absorbing infrared radiation. While an excitation of fundamental oscillations occurs in the mid infrared range of the light, the near-infrared spectrum of a substance shows overtone peaks and combination bands of molecular vibrations, mainly from functional groups like O-H, C-H and N-H (Ciurczak, 2001; Malley et al., 2004; Cécillon et al., 2009). This makes NIRS especially suitable for organic compounds (Weyer, 1985; Miller, 2001). Phosphates and other P compounds are hardly detectable by NIRS due to the weak P-O dipole moment (Malley et al., 2004). The detection of P compounds seems to be possible, if they are correlated with other NIRS-detectable soil properties, in particularly organic properties (Stenberg et al., 2010).

Each type of molecule has characteristic absorption bands for near-infrared radiation, but there is much interference and overlap between the overtone and combination oscillations. Therefore molecules cannot be identified by single peaks, the whole spectral information or at least several regions of the spectrum are needed to determine a molecule (Ciurczak, 2001; Günzler and Gremlich, 2003; Roberts et al., 2004).

The spectral region of NIR radiation ranges from 800 to 2500 nm wavelength, following directly the visible light region. In infrared spectroscopy, commonly the wavenumber

ν in cm^{-1} is used, which is the reciprocal of the wavelength λ.

$$\nu = \lambda^{-1}$$

Since the O-H bond has a strong influence on near-infrared absorption (Schmitt, 2000; Malley et al., 2004) ground samples were dried at 40 °C and measured under constant humidity conditions. For each soil sample, five spectra were taken with a Fourier Transform Mid- and Near Infrared combination instrument (Tensor 37, Brukeroptics, Ettlingen, Germany). Each spectrum is a mean of 64 individual scans over the range of 12 000 to 4000 cm^{-1} wave numbers with a resolution of 16 cm^{-1}. Model development was done with the OPUS 6.5 spectroscopy software (Brukeroptics, Ettlingen, Germany). The first derivative, vector normalization, or a combination of these two were used as data treatment for the partial least square regressions and applied to a variety of frequency ranges to find the best fit with the value of the respective component; several smoothing point values for the derivatives were tested, too. Calibration was performed with cross validation, a common approach for small data sets. Here, a defined number of samples, in our case one sample, were stepwise excluded from the calibration process. The rest of the samples were used to predict the excluded samples. This procedure was performed until all samples were excluded once, and the best models to predict all samples were found (Conzen, 2005). For each dataset, only 80 % of the samples were used for development of models, the remaining 20 % were left out for later external validation of the models to test their prediction quality. This is carried out with an automatic function in the Opus software (Conzen, 2005; Bruker Optik User Manual, 2006) selecting samples for each individual model equally over the whole range of each dataset, with min and max values always assigned to the calibration set and the samples second to min and max values always to the validation set.

Our initial intent was to generate a global prediction model for P concentration that integrated the whole variety of forest soil types. The aim was to test, if such a global model could be used to estimate P concentration of all BZE samples and for future inventories. Since this approach proved to be difficult, we also tried to develop NIRS models for sub-sets of the total sample pool with reduced variation in soil properties including P. We grouped the soil samples according to their specific characteristics and origins. Among others we divided the samples by soil depth, type of organic layer, dominant tree species, and soil type. We also grouped the soil samples into different classes characterized by their measured total P content, by the sum of P in all fractions, sum of all Po fractions as well as by organic C, clay, and sand content. The only classification of samples that yielded model qualities superior to that when using the whole dataset was the separation according to sample origins and soil type. To assess whether the prediction of P by NIRS depended on original properties of soil P or rather indirectly on properties of soil organic matter, we used correlation analyses to see whether the quality of NIRS models to predict P could be explained by the relationships between P and soil C and N.

As mentioned above, it was presumed that P bound to C or N could be modelled with better quality.

To address the hypothesis that the predictive quality of NIRS models increases with the homogeneity of sample sets, we finally established calibrations for sample populations of varying heterogeneity (Fig. 3):

1. a full dataset containing all soil samples with the greatest heterogeneity,
2. an almost equally heterogeneous BZE dataset comprising many different soil types,
3. the less heterogeneous BZE sub-set of “Brown Earths” soil samples, and
4. the relatively homogenous BEF-China sample set comprising soils from one soil type and from one small region.

The BZE Brown Earths dataset (set 3) with 82 samples was too small for a robust validation with external samples that were not used in the calibration. Still, we included it in our study, because it was the only meaningful and less heterogeneous subset of samples that could be separated from the whole BZE data set (set 2). The sizes of the sample sets 1 and 2 were comparable with those used in other studies to develop "global" models (Abrams et al., 1987; Shenk and Westerhaus, 1993; Gillon et al., 1999). Sample set 4 could be regarded as an extensive but local data set. A principal component analysis (Fig. 3) (OPUS 6.5 software) was carried out to assess spectral properties of the selected subsamples. The general spectral properties of the soil samples indicated that the BEF China sample set (set 4) was more homogenous than the BZE sample sets and clearly separated from the BZE sample set as a whole as well as from the subset BZE-"Brown-Earth". The spectral properties of the two subsets of BZE samples were not different.

To evaluate the prediction quality of NIRS models, the statistical parameters R^2 and the ratio of performance to deviation (RPD = ratio of standard error of prediction to SD) were used. The usefulness of these statistical parameters to characterize the quality of NIRS models has been discussed controversially (Chang et al., 2001; Williams, 2001; Malley et al., 2004; Zornoza et al., 2008). Especially for soil analysis, high values for RPD and R^2 are hardly achieved (Malley et al., 2004). To judge our RPD and R^2 values, we followed the classification suggested by Malley et al. (2004), who provided an overview and summary on this topic. We applied the following 4 levels to classify model quality:

- Level A: $R^2 > 0.95$ and RPD > 4, excellent calibrations, usable for all applications
- Level B: R^2 between 0.90 and 0.95, RPD between 3 and 4, successful calibrations usable for most applications some with caution, e.g. quality assurance
- Level C: R^2 between 0.80 and 0.90, RPD between 2.25 and 3, moderately successful calibrations, usable with caution, e.g. research
- Level D: R^2 between 0.70 and 0.80, RPD between 1.75 and 2.25, moderately useful calibrations, usable for screening of samples

Calibrations with lower values might still be useful for rough screening purposes (Chang et al., 2001).

All statistical analyses shown in this study are performed with SPSS Version 20.

3 Results

3.1 Soil Phosphorus concentrations

Total P concentrations were higher and showed a wider range in the BZE samples than in the BEF-China samples for all pools of P availability and individual fractions (Table 1). The sub group "Brown Earths" was characterized by a large variation in total P concentration (130 to 2200 mg kg^{-1}, as the sum of all Hedley fractions), which had a smaller range of values than the pool of all BZE samples but, as indicated by the SD, a similar variation in total P. The same applied to P in the labile, moderately labile, and stable pools. The mean percentage of organic P, here calculated as the sum of all Po fractions without the HCl conc. fraction, was higher in the BEF-China samples (57 %) than in the BZE and BZE "Brown Earths" samples (42 and 44 %). However, there was no difference in the range of organic P (10–70 % of the total) for the three datasets. The organic P fraction with the highest concentrations in all three datasets was the one extracted with NaOH (mean value BZE 155 mg kg^{-1}, BZE "Brown Earth" 196 mg kg^{-1}, BEF-China 35 mg kg^{-1}). The P concentrations in the $NaHCO_3$-extractable and the 1 M HCl-extractable Pi fraction in the BEF samples were so low as to fall within the measurement inaccuracy of the Hedley method.

3.1.1 NIRS models by P fractions

Initially, NIRS models were calibrated for both, the complete sample set as well as for three different subsets (BZE, BZE Brown Earths, and BEF-China). The global model for all samples produced no useful calibrations. The BZE model, which was developed for samples from different soils types, showed only for the P HCl conc. fraction a moderately useful calibration, while all other fractions could not be calibrated sufficiently well (Table 3). For all fractions except the inorganic NaOH, better calibrations were achieved in the BZE “Brown Earths” subset than in the complete BZE dataset. However, calibration models achieved D level quality only for two fractions (Po NaOH, P HCl conc.). The more homogenous BEF-China dataset yielded the best calibrations. Only the inorganic $NaHCO_3$ and the inorganic 1 M HCl fraction were, owing to the very low concentrations, not calibrated successfully. Calibrations to predict the Pi Resin, Po $NaHCO_3$, Pi NaOH and P residual fraction produced models of level D quality, while calibrations for the organic NaOH and the P HCl conc. fractions yielded models of level C quality. Overall, best calibration models were achieved for the BEF-China dataset especially for the organic P fractions extracted with $NaHCO_3$, NaOH, and the P HCl conc. fraction (Table 3).

Models providing level D calibrations were subsequently tested with a validation dataset comprising samples not included in the calibration. Whereas the validation of the level D calibration model of the BZE set for the HCl conc. P fraction was not successful, validation of this fraction in samples of the more homogenous subset BZE “Brown Earths” yielded a model quality of level C. Validation models for the P HCl conc. fraction in BEF soil samples achieved a level B quality (Fig. 4).

The validation of models for the Po $NaHCO_3$ ($R^2 = 0.72$, RPD = 1.87), Pi NaOH ($R^2 = 0.68$, RPD = 1.77) and P residual ($R^2 = 0.75$, RPD = 1.98) fractions of the BEF China dataset reached level D quality, while the model for the Pi Resin fraction could be validated at level C quality ($R^2 = 0.83$, RPD = 2.39). The validation of the model for the Po NaOH fraction reached level B ($R^2 = 0.91$, RPD = 3.23).

3.1.2 NIRS models by P pools

The calibration of models for the merged dataset (BZE + BEF) achieved only for the stable P pool a level D prediction, whereas the calibrations for the other pools did not produce any useful models (Fig. 5). We then calibrated models for each of the three P pools of different solubility for the three individual datasets BZE, BZE “Brown Earths” and BEF. For the two BZE datasets, the calibrations yielded similar results to our global calibration model. Only one level D calibration was achieved for the stable P pool. For the BEF China dataset, calibrations yielded one level D model for the labile P pool, whereas level C calibration models were obtained for the moderately labile and stable P pools.

Validation of the useful calibration models for the stable P pool in the three datasets BZE + BEF, BZE and BZE “Brown Earths” yielded a level D model ($R^2 = 0.79$, RPD = 2.16) for the complete set (BZE + BEF) as well as the BZE dataset ($R^2 = 0.73$, RPD = 1.91) and a level C model ($R^2 = 0.88$, RPD = 2.83) for the BZE “Brown Earths” dataset.

Validations for the BEF China datasets achieved a level C quality for the labile and the moderately labile P pool, and level D quality for the stable P pool (Fig. 6).

The relationships between the goodness of fit of calibration models for all individual P fractions and Spearman rank correlation coefficients of the relationship between the total organic carbon (a), total nitrogen (b) and the respective P fraction were best for the Po fractions for all datasets (Fig. 7). The BEF China dataset showed better results than the BZE datasets also for fractions that did not show a strong correlation between C and P or N and P. For the BZE datasets, model quality for organic P fractions was also inadequate despite reasonably strong relationships between C and P or N and P. The high model quality for P in the HCl conc. fraction could not be explained by relationships between C and P or N and P. If we disregard those P fractions for which Pi and Po cannot be reliably discerned (HCl conc. and residual P), the correlation coefficients between model quality as a dependent variable and the relationship between soil C or N and P in the respective Hedley fraction as an independent variable was 0.72 for C ($p < 0.001$) and 0.78 for N ($p < 0.001$).

4 Discussion

4.1 NIRS models for Hedley fractions and pools

Calibration and validation models of individual fractions achieved good to satisfactory results for some but not all individual P fractions. Generally, the accuracy and reproducibility of the reference method is of crucial importance for the quality of predictions with NIRS models (Williams, 2001). To increase reproducibility in our study, all samples were measured according to the same protocol in the same laboratory at the University of Freiburg. In addition, the strong agreement between the recovery of total soil P and the sum of all individual fractions indicated a high reproducibility of the method. This reproducibility, however, does not provide information about the distribution of Pi and Po within individual fractions. For the individual fractions, it is widely acknowledged that significant potential errors may occur owing to variation in alkalinity or acidity in the extracts leading to acid hydrolysis and precipitation of inorganic P. This can make it difficult to accurately distinguish between organic and inorganic forms of P and may thus lead to over- or underestimation of these forms within individual fractions (Magid et al., 1996; Condron et al., 2005; Turner et al., 2005; Tiessen and Moir, 2008; Condron and Newman, 2011). However, we achieved good reproducibility for Pi and Po in repeatedly analyzed samples for $NaHCO_3$ and NaOH fractionation steps (random quality check, data not shown).

Other than these methodological limitations of the Hedley fractionation method, the minimum P content of each fraction is also of importance. The P content in the Pi $NaHCO_3$ and 1 M HCl fractions of the soil samples from subtropical China were close to the detection limit. Therefore the reference data of these two factions could not be regarded as reliable and hence no valid calibration models with NIRS could be produced.

Using all Hedley fractions, the description of soil P availability becomes easily confusing. In this case up to eleven, twelve if total P is taken in account, different P values describe the P status of soil samples or forest sites. In addition, some fractions could not be calibrated owing to very low P concentrations or only with very low prediction quality. To reduce the number of variables and facilitate communication, we grouped the P fractions into pools according to their plant availability (Fig. 1) as is often found in the literature (e.g., Stevenson and Cole, 1999; Yang and Post, 2011, de Schrijver et al., 2012). Hence, in addition to individual Hedley fractions, we also modelled P content for the pooled fractions classified as labile, moderately labile, and stable. In case of the BEF China data set, pooling the fractions showed a slight increase for the quality parameters R^2 and RPD, but the quality of models remained at the same level. These pools incorporated the inorganic $NaHCO_3$ and 1 M HCl fractions, which could not be predicted individually, and thus facilitated a reasonable prediction of the total P content for the BEF China samples. While pooling these fractions does not reduce the work involved in reference analysis of the Hedley fractionation, it is still a significant reduction in the modelling process, reducing the number of models from 8 to 3 for each dataset.

4.2 Calibration of organic and inorganic fractions

The type of P in organic or inorganic form seems to be an important parameter for the quality of predictions of Hedley fractions with NIRS. Regardless of the datasets and sample origin, models predicting the organic P fractions performed better than those for inorganic P fractions (Table 3). The superior quality of models for organic P fractions is related to the underlying mechanisms generating NIR spectra, in which organic compounds can be more easily excited by the irradiation than inorganic ones. Similar results have been obtained for nitrogen (Ludwig et al., 2002). Spectral variation in relation to soil P content is often associated with organic matter or crystal water (Ben-Dor and Banin, 1995; Chang et al., 2001; Malley et al., 2005; Stenberg et al., 2010). Therefore, we also calibrated NIRS models for the sum of P in all organic fractions (data not shown). However, we could not observe any improvement for prediction of total organic P in comparison with single organic fractions or the pools. This might be caused to the large diversity in organic P compounds (Turner, 2008). In contrast to organic P fractions, the relationships between inorganic P fractions and other NIRS-detectable soil properties were obviously not strong enough to aid the prediction of inorganic P using NIRS.

The indifference in relationships between NIRS model quality and correlation coefficients for the relationship between P in Hedley fractions and soil C and N (Fig. 7) indicated that NIRS models are based on original properties of organic P and not simply a function of soil organic matter content. This corroborates the underlying assumptions of the Hedley fractionation that P in the individual organic fractions is of different availability owing to the different properties of the organic matter dominating the respective fraction. In turn, this indicates that total organic soil C and N can be used only to a limited extent to predict organic P in different fractions. For inorganic P fractions the relationships between soil C and N and P fractions and the NIRS model quality were, as expected, even poorer or non-existent (Fig. 7).

4.3 Homogeneity of datasets

The quality of predictions of P fractions depended on the homogeneity of individual datasets. The question of homogeneity has also been discussed in the use of global and local calibration models by Abrams et al. (1987) and Shenk and Westerhaus (1993), who found that global models were potentially as accurate as more local calibrations for mixtures of hay consisting of different plant species and origins. Variable results were obtained for calibrations of the total C, N and P between global and local models of heterogeneous plant material (Gillon et al., 1999). The global model, which combined all individual datasets of pine needle categories (needles on trees, fallen needles and litter), was more accurate or similar than the “local” individual datasets for each category of needles (Gillon et al., 1999). However, a decline in model quality was observed for global models predicting carbon. In contrast, a comparison of NIRS models for soil organic C, inorganic C and clay content showed a decreasing accuracy from local to global calibration models (Sankey et al., 2008). For our soil data sets, an increasing model quality with increasing heterogeneity of sample origin could not be observed. Also the general observation that an increase in the range of values leads to an increase in the robustness of NIRS models (Abrams et al., 1987; Shenk and Westerhaus, 1993) did not apply in our study. Our results indicated that regardless of the organic or inorganic origin or the availability of P, the quality of NIRS models to predict P was better for more homogenous than heterogeneous sets of soil samples. For example, reducing the soil samples from the nationwide forest soil monitoring program to the subset BZE "Brown Earths", we produced a more homogenous subset that improved model calibrations for all but the inorganic NaOH fraction. The most homogenous BEF China sample set produced even better calibration models than the BZE subset.

Since P is not "recognized" directly by near-infrared radiation but produces signals in the spectra that are related to P compounds, it appears that the signals for the same group of P compounds that relate to a specific Hedley fraction vary greatly among different soil types. For organic P, these groups of compounds are probably present in more than one fraction and the various extracts are unlikely to be either exhaustive or unique with respect to the target compounds (Turner et al., 2005). To our knowledge the chemical nature of the organic phosphorus within the operationally defined fractions is still poorly understood (Magid et al., 1996; Turner et al., 2005). The same may be said for different forms of inorganic P. This variation of P forms within Hedley fractions may be greatly reduced through restricting the development of NIRS models to comparable soil types. The possible over- and underestimation of inorganic and organic P stated above could also lead to a possible explanation for the dependency of homogeneity within the individual dataset.

5 Conclusions

The approach to predict soil P in Hedley fractions of different availability with NIRS can be regarded successful only when certain limitations are considered. NIRS models for prediction of individual inorganic P fractions were at best moderately useful but unsuitable for soil inventories. We found that the quality of NIRS models for prediction of P, for single fractions as well as for pools, depended on the homogeneity of sample sets.

The homogeneity may not only be related to the same soil types (improved models after grouping of soil types in the BZE subset), but also to the same geology that has a large influence on soil properties (better calibration models of the BEF China sample set – with the same geology – than the BZE subset originating from different geologies). The approach may therefore be well suited for large experiments that require a great number of spatial and temporal replication of samples within well-defined soil types. For large-scale, grid based soil inventories such as those conducted in the context of environmental monitoring programs for entire regions, like nation-wide soil surveys, it appears that NIRS-models to predict P fractions need to be developed for individual soil groups or other classes of samples according to specific soil properties. While the development of NIRS models represents a considerable initial investment, these efforts are likely to pay off only for large sample numbers and in repeated inventories.

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Table 1. Descriptive statistical parameters of soil P content (mg kg^{-1}) as the total sum of Hedley P fractions and in pools of different plant availability, grouped by data sets used for NIRS modelling.

Data Set	P Pool	*n*	Min	Mean	Max	SD	Skewness	Kurtosis
BZE all	total sum	282	57.8	564.0	2796.1	413.4	1.93	6.22
	labile		6.0	123.6	850.0	110.7	2.37	8.90
	moderately labile		8.1	296.7	2307.7	266.2	3.24	18.49
	stable		6.7	141.1	805.2	127.4	1.85	4.07
BZE “Brown Earths”	total sum	84	128.1	657.7	2178.0	440.59	1,23	1,739
	labile		11.0	166.3	850.0	146.89	2.06	5.56
	moderately labile		46.9	357.3	1227.0	256.9	1.16	1.44
	stable		6.7	134.3	534.3	118.4	1.43	1.88
BEF China	total sum	294	25.7	94.8	328.6	47.9	1.68	4.51
	labile		1.2	17.0	78.9	10.6	1.78	6.45
	moderately labile		10.8	43.7	161.2	21.8	1.67	5.63
	stable		10.8	34.1	174.8	23.1	3.01	11.84

Table 2. Descriptive statistical parameters of carbon ($g\,kg^{-1}$), nitrogen ($g\,kg^{-1}$) and pH (H_2O) in soil, grouped by data sets used for NIRS modelling.

		n	Min	Mean	Max	SD	Skewness	Kurtosis
BZE	C	282	0.21	42.91	178.00	36.31	1.24	1.07
	N		0.11	2.71	12.35	2.16	1.32	1.83
	pH		3.20	4.50	8.20	0.79	1.90	4.91
BZE "Brown Earths"	C	84	3.57	56.16	178.00	45.24	0.80	−0.32
	N		0.20	3.40	10.00	2.54	0.78	−0.20
	pH		3.41	4.43	7.75	0.66	2.72	11.33
BEF-China	C	294	3.42	30.92	118.10	17.18	1.37	2.99
	N		0.29	1.56	5.90	0.78	1.50	4.47
	pH		3.47	4.52	5.1	0.23	−0.67	1.69

Table 3. Quality pararmeters for NIRS model calibration (R^2, RPD) for all Hedley fractions in the three data sets: BZE, BZE "Brown Earths", and BEF-China.

Hedley Fraction	BZE		BZE "Brown Earths"		BEF-China	
	R^2	RPD	R^2	RPD	R^2	RPD
Pi Resin	0.26	1.16	0.51	1.44	0.77	2.08[1]
Pi $NaHCO_3$	0.08	1.04	0.19	1.10	0.48	1.39
Po $NaHCO_3$	0.61	1.60	0.63	1.64	0.78	2.13[1]
Pi NaOH	0.23	1.14	0.15	1.09	0.72	1.88[1]
Po NaOH	0.61	1.60	0.75	1.98[1]	0.82	2.35[2]
Pi 1 MHCl	0.30	1.19	0.38	1.26	0.34	1.23
P HCl conc.	0.72	1.88[1]	0.76	2.05[1]	0.85	2.57[2]
P residual	0.56	1.50	0.57	1.52	0.69	1.79[1]

[1] Model quality level D. [2] Model quality level C.

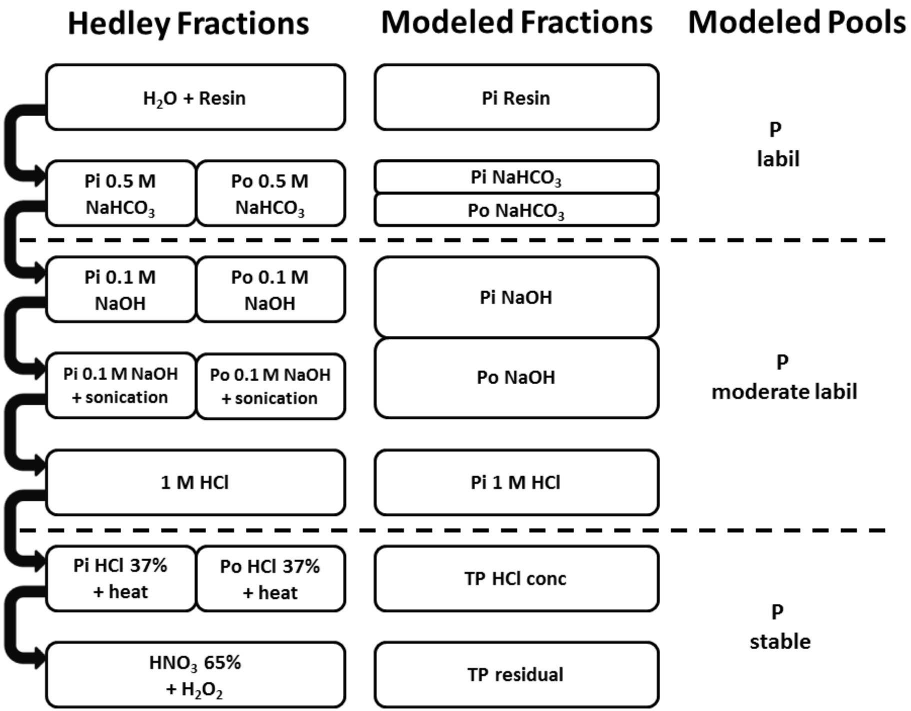

Figure 1. Sequential extraction scheme of Hedley fractionation modified by Tiessen, grouped by pools of availability; $NaHCO_3$, NaOH and HCl conc. steps provides both organic and inorganic compound for this fraction step.

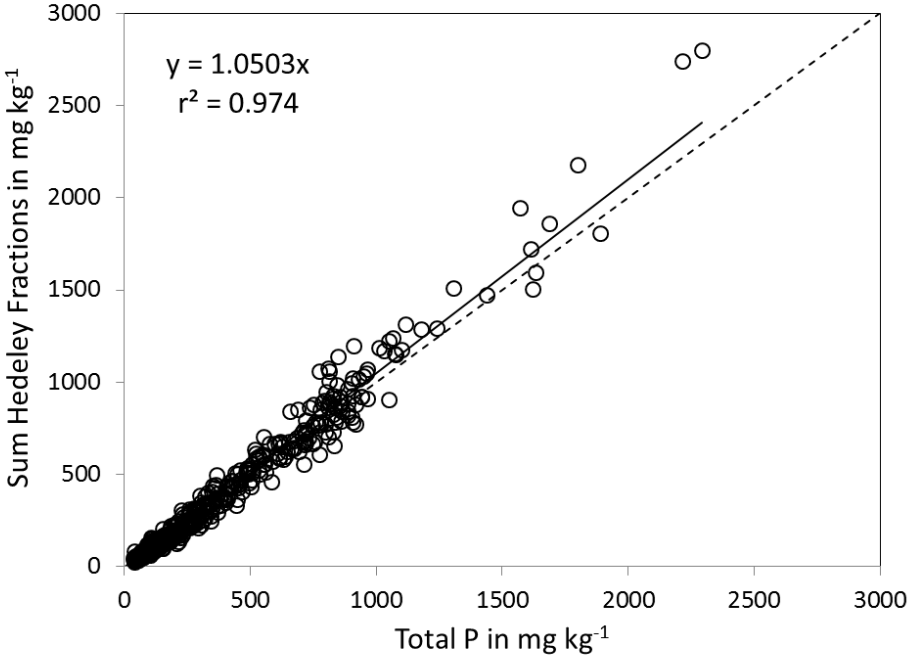

Figure 2. Relationship between the sum of recovered Hedley P fractions and independently determined total P (mg kg^{-1}) in soil samples.

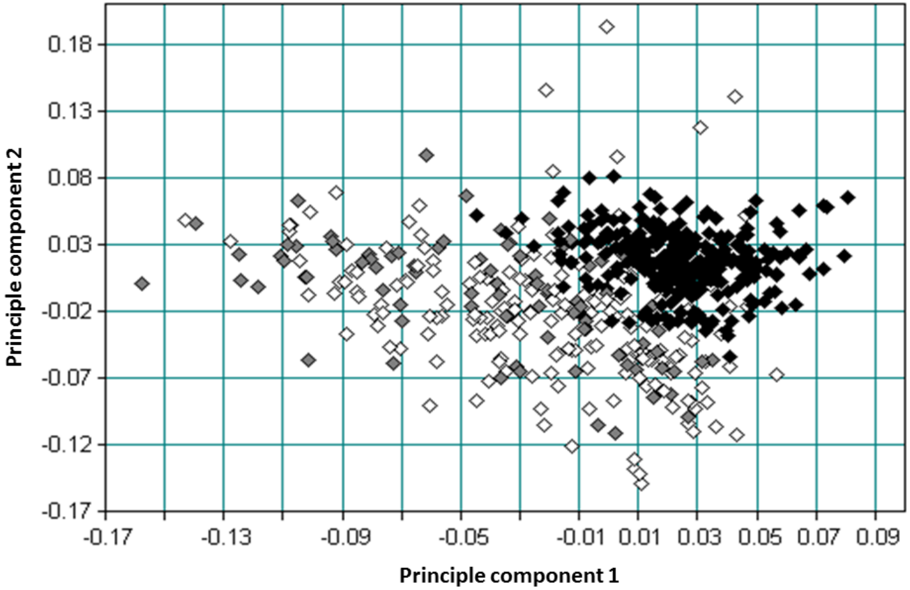

Figure 3. Score plot of principle component analysis (Principle component 1 vs. Principle component 2) for the three datasets BZE (white, set 2), BZE “Brown Earths” (grey, set 3) and BEF China (black, set 4).

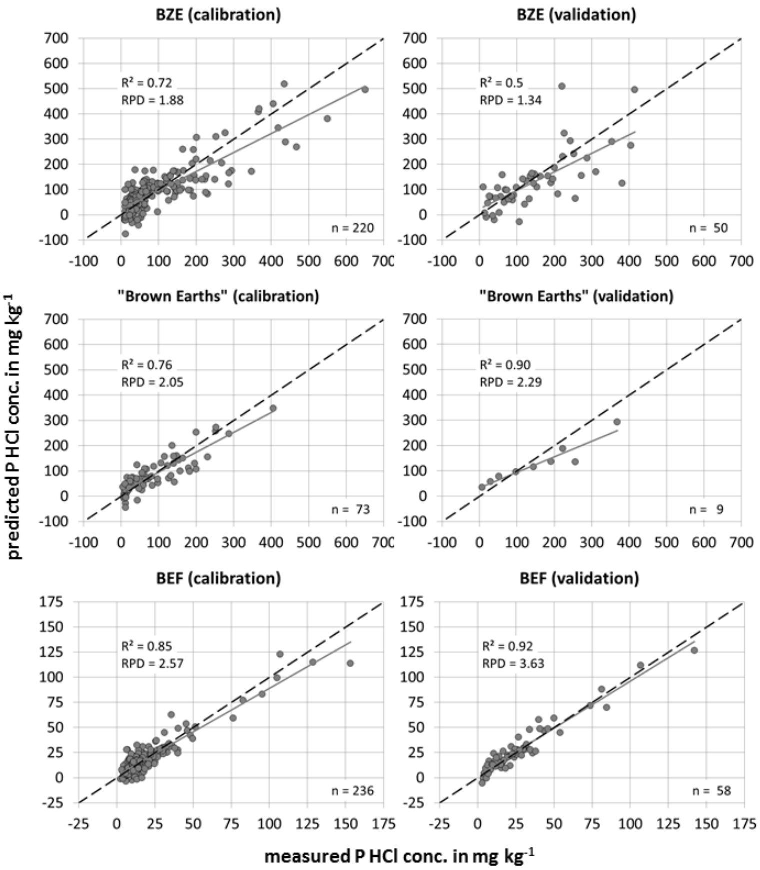

Figure 4. Calibration (left) and validation (right) for the P HCl conc. fraction of the three datasets BZE, BZE "Brown Earths" and BEF China (mg kg^{-1}), *x* axis measured, *y* axis predicted values, please note the difference in scale among graphs.

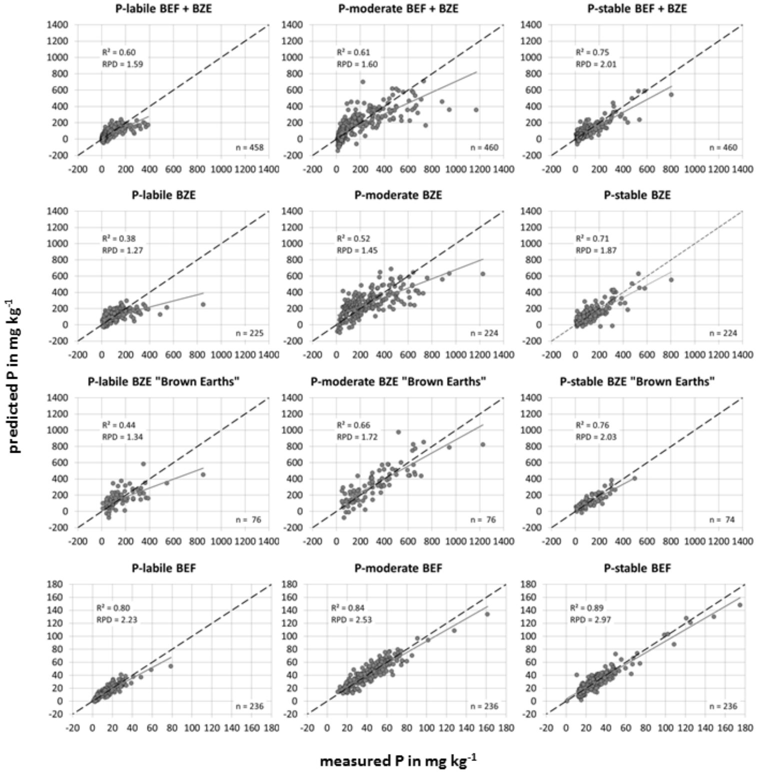

Figure 5. Calibration models for the four datasets BEF China + BZE, BZE, BZE "Brown Earths" and BEF China, pooled for labile, moderately labile (mod. labile) and stable phosphorus ($\mathrm{mg\,kg^{-1}}$), *x* axis measured, *y* axis predicted values, please note the difference in scales.

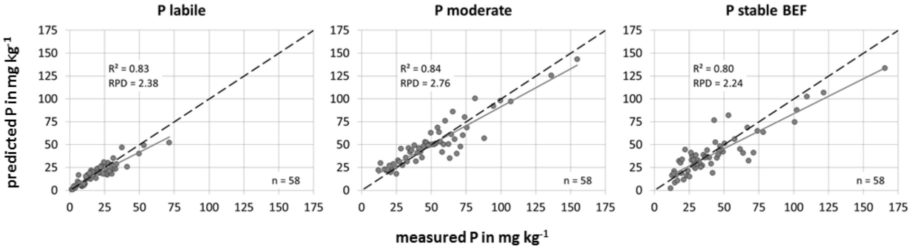

Figure 6. Validation for BEF China calibration models with external datasets pooled for labile moderately labile (mod. labile) and stable phosphorus (mg kg^{-1}), *x* axis measured, *y* axis predicted values.

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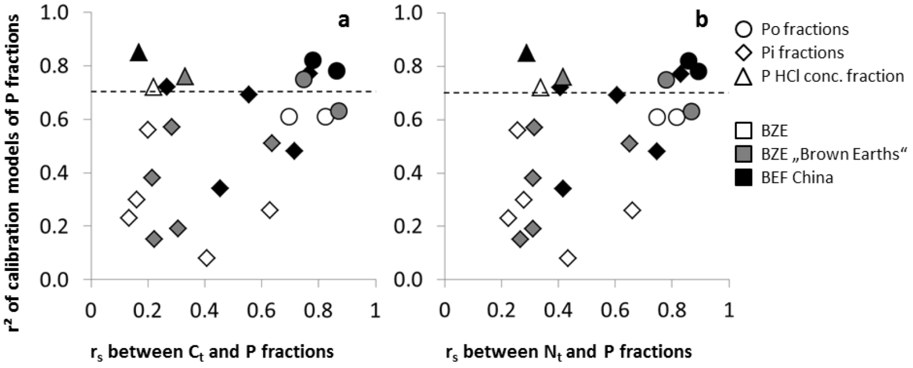

Figure 7. Relationship between the goodness of fit of calibration models for all individual P fractions and Spearman rank correlation coefficients of the relationship between the total organic carbon **(a)**, total nitrogen **(b)** and the respective P fraction (circles = organic fractions; squares = inorganic fractions;) in soils for all three datasets (black = BEF China; grey = BZE "Brown Earths"; white = BZE), dashed line indicates the minimum model quality of $r^2 = 0.7$.