

1 **ON-LINE MEASUREMENT OF SOIL PROPERTIES WITHOUT DIRECT**
2 **SPECTRAL RESPONSE IN NEAR INFRARED SPECTRAL RANGE**

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10

11 **Abstract**

12 So far, the majority of reports on on-line measurement considered soil properties with
13 direct spectral responses in near infrared spectroscopy (NIRS). This work reports on
14 the results of on-line measurement of soil properties with indirect spectral responses,
15 e.g. pH, cation exchange capacity (CEC), exchangeable calcium (Ca_{ex}) and
16 exchangeable magnesium (Mg_{ex}) in one field in Bedfordshire in the UK. The on-line
17 sensor consisted of a subsoiler coupled with an AgroSpec mobile, fibre type, visible
18 and near infrared (vis-NIR) spectrophotometer (tec5 Technology for Spectroscopy,
19 Germany), with a measurement range of 305 - 2200 nm to acquire soil spectra in
20 diffuse reflectance mode. General calibration models for the studied soil properties
21 were developed with a partial least squares regression (PLSR) with one-leave-out
22 cross validation, using spectra measured under non-mobile laboratory conditions of
23 160 soil samples collected from different fields in four farms in Europe, namely, Czech
24 Republic, Denmark, Netherland and UK. A group of 25 samples independent from the
25 calibration set were used as independent validation set. Higher accuracy was obtained
26 for laboratory scanning as compared to on-line scanning of the 25 independent
27 samples. The prediction accuracy for the laboratory and on-line measurements was

28 classified as excellent/very good for pH (RPD = 2.69 and 2.14 and $r^2 = 0.86$ and 0.78 ,
29 respectively), and moderately good for CEC (RPD = 1.77 and 1.61 and $r^2 = 0.68$ and
30 0.62 , respectively) and Mg_{ex} (RPD = 1.72 and 1.49 and $r^2 = 0.66$ and 0.67 ,
31 respectively). For Ca_{ex} , very good accuracy was calculated for laboratory method (RPD
32 = 2.19 and $r^2 = 0.86$), as compared to the poor accuracy reported for the on-line
33 method (RPD = 1.30 and $r^2 = 0.61$). The ability of collecting large number of data points
34 per field area (about 12800 point per 21 ha) and the simultaneous analysis of several
35 soil properties without direct spectral response in the NIR range at relatively high
36 operational speed and appreciable accuracy, encourage the recommendation of the
37 on-line measurement system for site specific fertilisation.

38

39 **1 Introduction**

40 During the last decade visible near infrared spectroscopy (vis-NIRS) is being
41 increasingly used to detect soil properties, with variable accuracy depending on several
42 factors (Kuang et al., 2012). The vis-NIRS is a simple, non-destructive and rapid
43 technique, needs no sample preparation for field applications, and can be used for the
44 laboratory, *in situ* (Viscarra Rossel et al., 2006a), and on-line measurements (Mouazen
45 et al., 2005). Furthermore, in some cases accuracy obtained is high and very similar to
46 that of conventional procedures (Viscarra Rossel et al., 2001). The technique allows
47 the assessment of primary properties with direct spectral responses, which are directly
48 affected by combinations and overtones of fundamental vibrations for organic
49 functional groups and water, particle size, and surface properties (Chang et al., 2001).
50 In a review paper, Stenberg et al. (2010) defined organic carbon (OC), total carbon
51 (TC), moisture content (MC) and clay minerals to have direct spectral response in the
52 NIR spectroscopy. In this context, it is possible to detect clay type and content, MC, OC
53 and TC with high accuracy (Volkan et al., 2010). Other soil properties without direct
54 spectral absorption features in the vis-NIR range (secondary properties) can be also

55 measured with good to moderate accuracy due to co-variation with one or more
56 primary properties (Stenberg et al., 2010). For both soil categories, colour plays an
57 important role in enhancing measurement accuracy. Good results have been reported
58 for cation exchange capacity (CEC), pH, extractable calcium (Ca_{ex}) and extractable
59 magnesium (Mg_{ex}) under non-mobile laboratory and *in situ* conditions but
60 underperformed those for properties with direct spectral responses in the NIR range,
61 e.g. OC, TC, MC and clay content (Kuang et al., 2012). According to the literature,
62 sodium (Na_{ex}) and potassium (K_{ex}) are among the most difficult properties to be
63 measured with the NIR spectroscopy (Malley et al., 1999, Chang et al., 2001, Zornoza
64 et al., 2008, Pirie et al., 2005, Dunn et al., 2002, Shepherd & Walsh, 2002, Islam et al.,
65 2003, Volkan et al., 2010; Mouazen et al., 2006). For the same soil property, laboratory
66 vis-NIR methods achieved higher accuracy as compared to measurement under field
67 soil conditions, particularly with on-line vis-NIR sensors (Stenberg et al., 2010; Kuang
68 et al., 2012).

69 The prediction accuracy achieved so far with the on-line vis-NIRS sensors available
70 today (Shibusawa et al., 2001; Mouazen, 2006; Christy, 2008) might be sufficient for
71 many applications in precision agriculture, since spatial and temporal variation of soil
72 properties is large relative to the precision of measurement (Shepherd and Walsh,
73 2002). However, similar to laboratory and *in situ* measurements, Kuang et al., (2012)
74 concluded that the best accuracy is achieved for soil properties with direct spectral
75 response, which is probably the reason why researchers using on-line vis-NIRS
76 sensors have focused mainly on soil properties with direct spectral responses (Shonk
77 et al., 1991; Mouazen et al., 2005; Brickley et al., 2010; Munoz and Kravchenko,
78 2011, Knadel et al., 2011). Mouazen et al. (2007) showed potential success for the on-
79 line vis-NIRS measurement of extractable and available P and pH, without proving the
80 accuracy to be of quantitative meaning. Although Mouazen et al. (2007) demonstrated
81 spatial similarities between measured and on-line predicted pH, no robust conclusions
82 on accuracy of measurement could be drawn. Later Mouazen et al. (2009) conducted

83 on-line measurement of available P with remarkable accuracy (RPD = 1.42; $r^2 = 0.62$).
84 To our knowledge none of the previous studies has reported on the on-line
85 measurement of CEC, Ca_{ex} and Mg_{ex} . In addition, no comparison was made between
86 laboratory and to on-line measurement of the named soil properties.

87 The aim of this paper is to evaluate the performance and accuracy of on-line
88 measurement of soil properties without direct spectral responses in the NIR
89 spectroscopy range, namely, CEC, pH, Ca_{ex} and Mg_{ex} . It also aims to compare the
90 prediction accuracy of these properties based on soil spectra collected under on-line
91 measurement conditions with those collected under laboratory non-mobile conditions.
92 Calibration models developed for several farms in Europe will be used to validate the
93 on-line measurement of these properties in one selected field in the UK.

94

95 **2 Materials and methods**

96 **2.1 Soil samples**

97 A total of 140 soil samples were used to develop general calibration models for the
98 prediction of pH, CEC, Ca_{ex} , and Mg_{ex} . These soil samples were collected from
99 different fields in six farms in four different European countries (Fig. 1 and Table 1). A
100 total of 25 samples were collected from one field in Mespol Medlov, A.S. farm (Czech
101 Republic), 20 samples from two fields in Bramstrup Estate farm (Denmark), 23 samples
102 from one field in Wageningen University (the Netherland), 25 samples from one field in
103 Ely farm (Cambridgeshire, UK), 17 samples from five different fields in Silsoe
104 experimental farm (Bedfordshire, UK) and 30 samples from fields 2 and 3 in Duck End
105 farm (Bedfordshire, the UK) (Table 2). Bulked samples were collected from the upper
106 soil layer (0-30 cm) in the spring of 2008 in the Mespol Medlov, A.S. farm and in the
107 spring of 2009 in Bramstrup Estate farm (Kuang and Mouazen, 2011). For the
108 remaining farms, soil samples were collected from the bottom of 15 cm deep trenches
109 opened by a subsoiler during the on-line vis-NIR measurement in the autumn of 2010

110 in Wageningen University, summer of 2009 in Silsoe experimental farm, spring of 2011
111 in Ely farm, and summer of 2011 in Duck End farm. These fields correspond to a large
112 diversity of soil textures, crops and landscapes (Table 1).

113 In order to validate the calibration models developed, on-line measurement was carried
114 out in field 1 in Duck End Farm (Table 2). During this measurement a total of 45
115 samples were collected for model development and validation. About 44 % of these 20
116 samples were added to the general calibration set (140 + 20 = 160 samples) to develop
117 the general calibration models of the selected four properties, whereas the remaining
118 25 samples were used as validation set for the validation of the general calibration
119 models based on non-mobile (laboratory) and on-line measured spectra of these 25
120 samples.

121 Approximately 200 g of each soil sample was kept deep frozen (-18 °C) until testing.
122 Before analysis, each sample was defrosted, carefully mixed and divided into two
123 portions, with one used for chemical analysis, and the other used for optical
124 measurement. Samples were stored in plastic bags at 4 °C during the analysis to avoid
125 losing humidity.

126

127 **2.2 Laboratory measurement of chemical soil properties**

128 Laboratory analyses of pH, CEC and base saturation, were performed at the soil
129 laboratory of the National Soil Resource Institute, School of Applied Sciences (NR-
130 SAS) of Cranfield University (Bedfordshire, the UK) using their standard procedures.

131 Soil pH was measured in a 1:5 soil:H₂O suspension following the **BS ISO 10390 (2005)**
132 for the determination of soil pH. In order to determine the CEC and exchangeable
133 cations (Na_{ex}, K_{ex}, Ca_{ex}, Mg_{ex}), the air-dried soil samples were first saturated with
134 respect to barium by adding 30 ml of barium chloride solution (Reagent Production Unit
135 (RPU) 10), after which 30 ml excess of 0.02 mol/l magnesium sulphate (RPU 11) was
136 added. This makes all barium present in the solution as well as adsorbed in

137 exchangeable sites to precipitate in the form of highly insoluble barium sulphate. As a
138 result, the exchangeable sites are occupied by magnesium. The surplus of magnesium
139 was determined by atomic absorption following the NR-SAS SOP 42/Version 1, based
140 on the **BS 7755 section 3.12 (1996)**, for the determination of the potential cation
141 exchange capacity and exchangeable cations using barium chloride buffered at
142 pH=8.1, which is identical to **ISO 13536 (1995)** (Table 3). Base saturation was
143 calculated as the equivalent sum of major base cations (Ca_{ex} , Mg_{ex} , K_{ex} and Na_{ex})
144 percentage of CEC (**Chodak et al, 2004**).

145

146 **2.3 Optical measurement**

147 **2.3.1 Optical measurement in laboratory**

148 For each soil sample a certain amount of soil was mixed up in a glass bowl. Stones
149 and plant residues were removed at this point. Three small cups of 1 cm deep and 3.6
150 cm in diameter were filled up with the same soil sample. The surface of the samples
151 was softly pressed and smoothed down with a spatula, simulating the effect of the
152 subsoiler smoothing of soil beneath the chisel during on-line measurement, which
153 increases the signal to noise ratio (**Mouazen et al., 2005**).

154 An AgroSpec mobile, fibre type, vis-NIR spectrophotometer (Tec5 Technology for
155 Spectroscopy, Germany) with a measurement range of 305 - 2200 nm was used to
156 measure soil spectra in diffuse reflectance mode. A 100 % ceramic was used as the
157 white reference, which was scanned once every 30 minutes. Optical scanning was
158 conducted on non-treated, fresh soil samples to simulate field measurement conditions.
159 A total of ten scans were performed for each of the three plates prepared for each soil
160 sample. The resulted thirty spectra were averaged into one spectrum for each sample
161 (**Kuang and Mouazen, 2011**). This averaged spectrum was used for spectra pre-

162 treatment and model development. All calibration (160) and validation (25) samples
163 were scanned in the laboratory.

164

165 **2.3.2 On-line vis-NIR measurement**

166 The on-line spectra were collected along parallel measurement lines in the field 1 in the
167 Duck End Farm in the UK (Fig. 2). Detailed information about this field is shown in
168 Table 4. The same vis-NIR spectrophotometer used for laboratory measurement
169 (AgroSpec) was used for on-line measurement. The on-line sensor developed by
170 **Mouazen (2006)** was used to carry out on-line measurement. The subsoiler makes a
171 trench in the soil, whose bottom is smoothed by the subsoiler itself, due to the
172 downwards vertical forces. The optical probe protected in a steel lens holder was
173 appended to the backside of the subsoiler chisel to measure soil spectra in diffuse
174 reflectance mode from the smoothed bottom of the 15 cm deep trench created by
175 the subsoiler chisel. The subsoiler retrofitted with the optical probe was attached to a
176 frame, which was mounted onto the three point linkage of a tractor (Fig. 3). The
177 spectrophotometer was IP 64 protected for harsh working environments. A differential
178 global positioning system (DGPS) (EZ-Guide 250, Trimble, USA) was used to record
179 the position of on-line measured spectra with sub-meter accuracy. A Panasonic semi-
180 rugged laptop was used for data logging and communication. The spectrophotometer,
181 laptop and DGPS were powered by the tractor battery.

182

183 **2.4 Pre-processing of spectra**

184 Several spectra pre-processing were tested and the best performing one was kept. The
185 selection criteria of any pre-processing were the largest coefficient of multiple
186 determination (r^2) and residual prediction deviation (RPD), which is the ratio of standard
187 deviation (S.D.) of the prediction data set to root mean square error of prediction

188 (RMSEP) and the smallest RMSEP. Spectra pre-processing and establishment of
189 calibration models of different properties were done by Unscrambler 7.8 software
190 (Camo Inc., Oslo, Norway). To remove noise at edges of spectra, soil spectrum was
191 first abridged to 400 – 2100 nm for each sample. After noise was removed, spectra
192 were reduced by averaging three successive wavelengths in the visible range (400 -
193 1000 nm) and six successive wavelengths for the NIR region (1000 - 2100 nm).
194 Averaging over wavelengths was used to decrease the number of wavelengths and to
195 smooth the spectrum (Nicola et al., 2007). Maximum normalization was followed, which
196 is typically used to get all data to approximately the same scale, or to get a more even
197 distribution of the variances and the average values. This method attempted to remove
198 the effects of scattering by linearising each spectrum to some 'ideal' spectrum of the
199 sample, which, in practice, corresponds to the average spectrum (Nicola et al., 2007).
200 The maximum normalization 'polarizes' the spectra. The peaks of all spectra with
201 positive values are scaled to +1, while spectra with negative values are scaled to -1.
202 The peaks of these spectra were scaled to +1, since all soil spectra in this study had
203 positive values (Mouazen et al., 2005). The maximum normalization was selected
204 because it provided better results for all properties considered compared with other
205 pre-processing tested. Spectra were subsequently subjected to Savitzky–Golay first
206 derivation (Martens and Naes, 1989). This transformation procedure generally
207 intensifies the absorption characteristics indicative of soils properties, and diminishes
208 variation among spectra (Volkan et al., 2010). This method enabled the computation of
209 the first or higher-order derivatives, including a smoothing factor, which determines
210 how many adjacent variables should be used to estimate the polynomial approximation
211 used for derivatives. A second-order polynomial approximation was selected with a 2:2
212 smoothing factor. A 2:2 Savitzky-Golay smoothing was carried out after the first
213 derivative to remove random noise from spectra (Kuang and Mouazen, 2011).
214

215 **2.5 Establishment of calibration models**

216 The pre-processed spectra and the results of laboratory chemical analyses were used
217 to develop calibration models for all studied properties. Before partial least squares
218 regression (PLSR) analysis, the 160 calibration samples (Tables 1 & 2) were divided
219 into calibration (85 % of samples) and prediction sets (15 % of samples). Further
220 validation of developed models was done using the 25 samples collected in the field 1
221 in Duck End farm, which was designated as independent validation set.

222 To develop calibration models, especial attention should be paid in the selection of
223 calibration and validation sets. The distribution and size of the calibration data set must
224 cover the entire range of concentration of a soil property examined. To build a robust
225 calibration model, validation of model developed has to be carried out using validation
226 samples, which were not used for model development. This means that validation
227 samples of the independent validation set (25 samples collected from the field 1 in the
228 Duck End farm) should not be used for the development of calibration models in cross-
229 validation, avoiding this way any influence in the prediction capacity of the model
230 selected and the consequent overestimation (Brown et al., 2005). The same samples
231 of calibration and validation were selected for each property. A previous threshing of
232 samples was executed to get the wider range of values and spectra variation in the
233 calibration set. Calibration and validation samples were then selected randomly.
234 Performing this way a calibration data set was set to cover the whole range of
235 concentration for the different soil properties examined.

236 The most used multivariate methods to develop calibration models are based on linear
237 regressions. Mainly, stepwise multiple linear regression (SMLR), principal component
238 regression (PCR), and PLSR (Stenberg et al., 2010) are used. The PLSR with leave-
239 one-out cross-validation was carried out using Unscrambler 7.8 software (Camo Inc.,
240 Oslo, Norway) to generate the calibration models relating soil independent variables
241 (wavelengths) of the diffuse reflectance spectra to each soil parameter. PLSR performs

242 particularly well, compared with other multivariate statistical methods, when there is a
243 high dimensional correlation between variables, which is the case for soil spectral data
244 (Volkan et al., 2010). Also, PLSR is favoured because it requires fewer components to
245 explain the variance in the response, due to the relation that this method establishes
246 between response and predictor variables, and its results are more interpretable
247 (Stenberg et al., 2010)

248 The number of latent variables for a model was determined by examining a plot of
249 leave-one-out cross-validation residual variance against the number of latent variables
250 obtained from PLSR. The latent variable of the first minimum value of residual variance
251 was selected (Brown et al., 2005). The residual sample variance and predicted vs.
252 measured plots were assessed for outliers determination after running the PLSR.
253 Outliers may be induced by typing errors, file transfer, interface errors, sensor
254 malfunctions and fouling, poor sensor calibration, bad sampling or sample
255 presentation, etc. (Nicola et al., 2007). Samples located individually far from the zero
256 line of residual variance together with a far position from the trend line in the predicted
257 vs. measured plot were considered as outliers and excluded from the analysis. A
258 maximum of 5 % of the entire samples was accepted as the maximum number of
259 outliers to be removed (Kuang and Mouazen, 2011).

260

261 **2.6 Performance assessment of calibration models**

262 Prediction accuracy of a PLSR model was determined by the RMSEP, r^2 and RPD. The
263 criteria adopted for RPD classification (Viscarra Rossel et al., 2006b) was as follows:
264 RPD < 1.0 indicates very poor model/predictions and their use is not recommended;
265 RPD between 1.0 and 1.4 indicates poor model/predictions where only high and low
266 values are distinguishable; RPD between 1.4 and 1.8 indicates fair or moderately good
267 model/predictions which may be used for assessment and correlation; RPD values
268 between 1.8 and 2.0 indicates good model/predictions where quantitative predictions

269 are possible; RPD between 2.0 and 2.5 indicates very good, quantitative
270 model/predictions, and RPD > 2.5 indicates excellent model/predictions. This
271 classification system was adopted in this study.

272

273 **3 Results and discussion**

274 For robust modelling of the vis-NIR spectral data, the selection of calibration set should
275 be carefully done so that to be representative of the samples used for validation. The
276 range for sample concentrations in the prediction (Table 5) and independent validation
277 (Table 6) sets is smaller and within the corresponding range for the calibration set
278 (Table 5) for all properties. This confirms that variation in the prediction and
279 independent validation sets are accounted for in the calibration set.

280 Since samples of Ely field were of excessively high exchangeable Ca_{ex} and Mg_{ex}
281 values, the 25 samples from Ely field were disposed during the development of the
282 calibration models for these two properties, as these might negatively affect the
283 prediction accuracy of the corresponding models.

284

285 **3.1 Evaluation of general calibration models**

286 Examining the results of the prediction set (Table 7), reveals that best results are
287 achieved for Mg_{ex} ($r^2 = 0.88$; RPD = 2.55) and pH ($r^2 = 0.86$; RPD = 2.37). Less
288 accurate estimations were obtained for CEC ($r^2 = 0.72$; RPD = 1.70) and Ca_{ex} ($r^2 =$
289 0.76 ; RPD = 1.87). According to the classification based on RPD proposed by [Viscarra](#)
290 [Rossel et al. \(2006b\)](#), the prediction accuracy in the prediction set is excellent and very
291 good for Mg_{ex} and pH, respectively, good for Ca_{ex} and moderately good for CEC. These
292 results are in line with those found in the literature. Comparing with other studies
293 reported in the literature under laboratory measurement condition ([Shepherd and](#)
294 [Walsh, 2002](#); [Cohen et al., 2005](#); [Mouazen et al., 2006](#); [Viscarra Rossel and Behrens.,](#)

295 2010), the model performance for pH in the prediction set is among the best models (r^2
296 = 0.50 - 0.97; RMSEP = 0.04 - 1.43; RPD = 0.57 - 2.39). Similar conclusion can be
297 drawn for the prediction of Mg_{ex} , with overall results reported in the literature for r^2 of
298 0.53 - 0.91; RMSEP of 0.03-38.36 cmol kg⁻¹ and RPD of 0.48 - 2.54 (Cozzolino and
299 Moron, 2003; Groenigen et al., 2003; Udelhoven et al., 2003; Wetterlind et al., 2010).
300 Almost the same results as those achieved in this study were reported by Dunn et al.
301 (2002), when analysing pH for the top soil of 0 - 10 cm (r^2 = 0.80, RPD = 2.3) and Mg_{ex}
302 (r^2 = 0.85, RPD = 2.7). The models for the other two properties are less accurate, as
303 compared with other values reported in the literature for Ca_{ex} (r^2 = 0.07-0.95; RMSEP =
304 0.66 - 52.90 cmol kg⁻¹; RPD = 0.60-2.75) (e.g. Cozzolino and Moron, 2003; Cohen et
305 al., 2005; Mouazen et al., 2006; Zornoza et al., 2008) and CEC (r^2 = 0.13 - 0.90;
306 RMSEP = 1.22 - 10.43 cmol kg⁻¹; RPD = 0.60 - 2.7) (e.g. Ben-Dor and Banin, 1995;
307 Chang et al., 2001; Mouazen et al., 2006; Brown et al., 2007; Awiti et al., 2008). Islam
308 et al., (2003), reported similar results for CEC (r^2 = 0.64, RPD = 1.6), using a separate
309 validation set to test the performance of calibration models developed. However, these
310 accuracies can still be considered as good and useful for quantitative predictions.

311

312 3.2 Comparison of laboratory and on-line measurement accuracy

313 In order to compare the performance of the general calibration models for the
314 prediction of studied soil properties between laboratory and on-line scanned spectra,
315 the independent validation set (25 samples) collected from the field 1 in Duck End farm
316 was used. Generally, smaller accuracies are observed when using soil spectra
317 collected under on-line measurement conditions, as compared to that for spectra
318 collected under laboratory non-mobile scanning conditions (Table 7). Results confirm
319 that the predictions of the laboratory and on-line measurements were classified as
320 excellent/very good for pH (RPD = 2.69 and 2.14 and r^2 = 0.86 and 0.78, respectively),

321 and moderately good for CEC (RPD = 1.77 and 1.61 and $r^2 = 0.68$ and 0.62 ,
322 respectively) and Mg_{ex} (RPD = 1.72 and 1.49 and $r^2 = 0.66$ and 0.67 , respectively). For
323 Ca_{ex} , very good accuracy was calculated for laboratory method (RPD = 2.19 and $r^2 =$
324 0.86), as compared to the poor accuracy for the on-line method (RPD = 1.30 and $r^2 =$
325 0.61).

326 There is little literature about the on-line prediction of secondary soil properties e.g.
327 properties without direct spectral responses in the NIR spectroscopy. Soil pH was the
328 most successfully measured property with on-line vis-NIR sensors, with all reports
329 show less accurate on-line predictions than the ones achieved in the current study ($r^2 =$
330 0.78) with r^2 values of 0.62 (Christy, 2008) and 0.61 (Shibusawa et al., 2001). Only
331 comparison between measured and predicted pH maps was provided by Mouazen et
332 al. (2007), showing similar trends of spatial distribution. The low prediction accuracy
333 obtained in this study for on-line Ca_{ex} might be attributed to the uneven distribution of
334 sample concentration over the entire concentration range. In spite of the wide range on
335 concentration, the majority of samples have low values for Ca_{ex} while there is a small
336 group of samples with very high values (Fig. 4). Thus, there is a gap of values between
337 both groups, hindering the creation of a robust calibration model. Similar comment can
338 be made for laboratory scanned spectra (data not shown). Similar trend is observed for
339 Mg_{ex} with a lower impact on the accuracy for both laboratory non-mobile and on-line
340 measurement. To reduce this effect samples from Ely field (UK), with the highest
341 values for Ca_{ex} and Mg_{ex} , were removed during the development of calibration models,
342 which led to the results shown in Table 7 and Figure 4. In the future, it is recommended
343 to consider new samples with Ca_{ex} and Mg_{ex} values covering the gap in the
344 concentration range for the development of more robust calibration models. The low
345 accuracy in predictions of the Ca_{ex} model could also be related with the extraction
346 method selected. This method might be inappropriate for Ca_{ex} detection in
347 predominantly calcareous samples.

348

349 3.3 Analysis of error

350 3.3.1 Histogram of error

351 The histogram of normal distribution plots of error was calculated by subtracting
352 predicted from measured values for each property using 25 samples of the
353 independent validation set (Tabl 8). It can be clearly observed that the mean, variance
354 and SD values are much larger with laboratory scanned than with on-line scanned
355 spectra. This is a clear sign to support the conclusion that accuracy decreases during
356 on-line measurement due to the ambient conditions (e.g. noise, vibration, stones, plant
357 roots, and a spectrum position with a corresponding soil sample) (Mouazen et al.,
358 2007; Stenberg et al., 2010). However, under laboratory scanning conditions all these
359 ambient conditions affecting accuracy are eliminated.

360 3.3.1.1 Histograms of error for pH

361 The histogram plot of normal error distribution for pH prediction using laboratory
362 scanned spectra is normally distributed around 0 (Figure 5a), with slight skewness
363 (0.392) towards the positive side, indicating slight overestimation. However, for on-line
364 prediction, a smaller skewness (0.024) can be observed (Table 8). Around 76 % and
365 64 % of laboratory and on-line predictions, respectively, are with smaller error than 0.3
366 in absolute values, which is smaller than 12 % of the normal pH range for agricultural
367 soils (4 - 9) (USDA, 1998). Furthermore, the range of prediction error is larger for on-
368 line prediction (-1.003 to 1.122), as compared to laboratory prediction. The smaller
369 range of prediction error in addition to the larger portion of small error than 0.3 (76 %)
370 of laboratory scanned spectra suggests the better performance of the general pH
371 model for prediction based on laboratory than on-line scanned spectra.

372 **3.3.1.2 Histograms of error for CEC**

373 Similar to pH, the histogram plots of CEC error for both laboratory and on-line
374 predictions show normal distributed around 0 (Figure 5b), with skewness values of -
375 0.004 and -1.201, respectively (Table 8). Around 64 % and 76 % of laboratory and on-
376 line predictions, respectively, are with smaller error than 1.1 cmol+/kg, which are
377 smaller than 4.4 % of the normal CEC range for agricultural soils (CEC = 0 cmol+/kg
378 for sandy soils to about 50 cmol+/kg for clay soils (Mengel and Kirkby, 1982). This
379 surprisingly shows a bigger proportion of error around 0 for on-line prediction, as
380 compared the laboratory prediction. However, the range of error was larger for on-line
381 prediction than for laboratory prediction (-3.908 to 2.483 cmol+/kg). This might be
382 attributed to difficulties associated with matching position of a soil sample collected for
383 laboratory chemical analysis and the corresponding spectrum collected during on-line
384 measurement (Mouazen et al., 2007).

385 **3.3.1.3 Histograms of error for Ca_{ex}**

386 The normal distribution plot of error for Ca_{ex} prediction using laboratory scanned
387 spectra (Figure 5c) is clearly skewed towards the negative side of the plot. This
388 skewness is larger for on-line (skewness = -0.523) than for laboratory (skewness = -
389 0.010) predictions (Figure 5c, Table 8). About 80 % and 52 % of laboratory and on-line
390 predictions, respectively, are with smaller error than 5.5 cmol+/kg in absolute values,
391 which are smaller than about 9 % of the Ca_{ex} range present in the samples. This
392 confirms that laboratory prediction of Ca_{ex} is more accurate than the on-line prediction,
393 which is supported by a larger range of error for the on-line, as compared to the
394 laboratory prediction (-21.911 to 9.025 cmol+/kg).

395 **3.3.1.4 Histograms of error for Mg_{ex}**

396 The normal distribution plot of error of Mg_{ex} of laboratory predictions presents a rather
397 normal distribution of error around 0. However, this is clearly skewed towards the
398 negative range when on-line spectra are used (Figure 5d, Table 8). About 56 % and 48
399 % of laboratory and on-line predictions, respectively, are with smaller error than 0.17
400 cmol+/kg in absolute values, which are a smaller error than about 4.7 % of the Mg_{ex}
401 range present in the samples. This indicates that as for pH and Ca_{ex}, the prediction of
402 Mg_{ex} is more accurate and stable when laboratory scanned spectra are used, as
403 compared to on-line measurement. This did not prove clearly for CEC, although the
404 trend is similar to the other three properties.

405 The above discussion about histogram plots of error and accuracy analysis confirms
406 that calibration models developed with laboratory scanned spectra perform better when
407 validated with laboratory measured spectra, as compared to on-line measured spectra.
408 However, in comparison with laboratory chemical and vis-NIR analyses, the on-line
409 measurement of soil properties enables the collection of high number of data points
410 (around 12.800 readings for 21 ha of the field 1), with average of around 2 points per
411 metre travel distance. This large amount of data allows the spatial interpolation to
412 estimates values for un-sampled points in the field. Then, the possibility to predict
413 several soil properties from the same spectrum, the opportunity to create maps from
414 this large amount of information and its utilisation for site specific land management
415 within the field, suggest the on-line measurement of soil properties as a valuable
416 measuring technique.

417

418 **4 Conclusions**

419 This paper reports on the performance of a vis-NIR spectroscopy-based on-line sensor
420 for the prediction of soil properties without direct spectral response in the NIR range,
421 namely, pH, CEC, Ca_{ex} and Mg_{ex}. It also compares prediction accuracy of these

422 properties between on-line and non-mobile laboratory scanning. The results obtained in
423 this study allow the following conclusions to be drawn:

424 1- The on-line measurement system enabled the simultaneous measurement of
425 several soil properties without direct spectral responses in the NIR spectroscopy
426 across a field.

427 2- General calibration models, developed with samples collected from fields in
428 different European countries are a successful procedure for the calibration of the on-
429 line vis-NIR sensor for the prediction of pH, CEC and Ca_{ex} and Mg_{ex} .

430 3- Higher accuracy was obtained for predictions using laboratory scanned, as
431 compared to on-line scanned spectra. The laboratory and on-line predictions were
432 classified as excellent/very good for pH (RPD = 2.69 and 2.14 and $r^2 = 0.86$ and
433 0.78, respectively), and moderately good for CEC (RPD = 1.77 and 1.61 and $r^2 =$
434 0.68 and 0.62, respectively) and Mg_{ex} (RPD = 1.72 and 1.49 and $r^2 = 0.66$ and 0.67,
435 respectively). For Ca_{ex} , very good accuracy was calculated for laboratory method
436 (RPD = 2.19 and $r^2 = 0.86$), as compared to the poor accuracy for the on-line
437 method (RPD = 1.30 and $r^2 = 0.61$).

438 4- The histogram plots of error proved the general calibration models developed with
439 laboratory scanned spectra to perform better when used to predict the studied soil
440 properties using laboratory scanned spectra, as compared to on-line scanned
441 spectra.

442 5- The ability of continuous data gathering with the on-line soil sensor at a relatively
443 high operational speed (about 3 km/h) with very good to moderate accuracy
444 obtained for some of the properties investigated (e.g. pH, CEC and Mg_{ex}), suggest
445 the recommendation of the on-line soil sensor for site specific fertilisation.

446 Further research is needed to upgrade the calibration models of pH, CEC, Ca_{ex} and
447 Mg_{ex} , developed in this study using samples collected from a larger number of fields
448 and countries with even distribution of concentrations along the entire concentration

449 range encountered in agricultural soils. This is recommended to improve the prediction
450 accuracy and robustness of models developed for studied soil properties.

451

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453

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