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Assessment of error sources in measurements of field pH: effect of operator experience, test kit differences and time-of-day

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14 Abstract

Various methods exist to measure soil pH, and while there is general agreement between existing 15 published laboratory and field based methods, the latter are subject to uncertainties including test kit 16 reliability, accuracy, precision and environmental factors. The contribution of this study is to quantify 17 three uncertainties that affect the conversion between field pH and laboratory pH measurements, 18 19 namely operator experience, choice of test kit and the time-of-day for measurement. Soil samples 20 from western Victoria, representing the pH range 4.5 to 10.0, were used in a randomised complete 21 block design with ten assessors split into two groups representing experienced and inexperienced 22 users. Statistical analysis of laboratory and field pH was based on using the Maximum Likelihood 23 Functional Relationship (MLFR) to determine if there was any bias between the two methods. 24 Significant differences were found between experienced and inexperienced users, and between test 25 kits.

Keywords: bias, relationship, Maximum Likelihood Functional Relationship (MLFR), impurities,
harmonization.

29

30 Introduction

Soil pH is the most frequently measured soil chemical property and provides invaluable background context to understanding chemical, physical and biological interactions and behaviours of soil and regolith with the biosphere and hydrosphere. Not only does pH have a critical role, as the expression of acidity or alkalinity and its impact on the availability and solubility of nutrients, it is also used for soil classification purposes, land use and land capability assessment and for modelling and understanding of agro-ecosystems.

37 Internationally there are numerous methods used to measure soil pH in field and laboratory 38 environments. In the laboratory, different ratios of soil and water or saline solutions are used. 39 Historically, in Australia, laboratories have measured pH in suspensions of soil and water by shaking 40 one part soil with 5 parts water for one hour (ISO 10390:2005; Method 4A1 in Rayment and Lyons, 41 2011). To better account for seasonal variability in insoluble salts due to rainfall or management 42 interventions, such as fertilizer addition (White 1969), water was supplemented with a weak salt solution, i.e. 0.01 M CaCl₂ (Method 4B1 in Rayment and Lyons, 2011). Arguably, laboratory pH 43 44 methods are the most reliable in comparison to field pH procedures; however, field based pH assessment 45 is rapid, inexpensive and results are instantly available to users, such as soil scientists, extension and advisory providers. 46

Field measurement of soil pH (hereon referred to as field pH) has been in use for 100 years, with methods required to be rapid, accurate, cheap and easily ascertained (Wherry 1920; Mason and Obenshain 1939). The sequential development of pH measurement includes methods that added salt solution to the soil (e.g. CaCl₂ or KCl) and those that added water to the soil and observed colour changes of indicators as related to concentrations (Wherry 1920). As field methods evolved, further comparison studies were undertaken to assess the usefulness of indicator methods in comparison with standard electrometric laboratory methods (Mason and Obenshain 1939). In Australia, enhancements to the makeup of indicator solution and methodology to apply barium sulphate onto a soil-indicator
paste (Raupach 1950; Raupach and Tucker 1959) led to the establishment of the colorimetric procedure
(Method 4G1 in Rayment and Lyons, 2011) that is still widely used today.

Field pH provides a simple, expedient and reliable approach to measuring pH for soil survey and 57 58 advisory services at various scales (Raupach and Tucker 1959; National Committee on Soil and Terrain 59 2009). Measurement of field pH using the colorimetric method of Raupach and Tucker (1959) has been 60 undertaken as standard practice in soil and land surveys across Australia for over 60 years. Extensive 61 collections of field pH measurements exist in state, territory and national databases, such as the 62 Victorian Soil Information System (VSIS, Hunter et al. 2010) and Australian Soil Resource Information 63 System (ASRIS, www.asris.csiro.au). Also contained within these databases are less frequent 64 companion sets of laboratory pH observations for pH in 1:5 soil-to-water suspension (hereon referred 65 to as pH_w or lab pH), and with 0.01M CaCl₂ extract.

66 Complementary field and laboratory measurements of soil pH on samples enable comparison of these 67 methods and evaluation of method performance. Comparative studies of various pH measurement 68 modalities have been carried out in the past (Mason and Obenshain 1939; Steinhardt and Mengel 1981; 69 Slattery and Ronnfeldt 1992). It has been demonstrated that there is reasonable agreement between lab 70 pH and field pH, measured from the same soil sample where a single operator was responsible for field 71 measurements (Baker et al. 1983). Steinhardt and Mengel (1981) specifically evaluated the performance 72 of a colorimetric indicator field method against the laboratory method for determining the accuracy of 73 predicting soil pH. However, while the authors identified some of the potential error sources that result 74 in variation between field and laboratory pH methods, the scope of this and early studies failed to 75 investigate factors affecting the strength of agreement between different methods of measuring pH for 76 extremely acid to alkaline soils.

Globally, there is a current focus on the delivery of digital soil maps (McBratney et al. 2003) exploiting
available legacy soil data (Carré et al. 2007) for initiatives such as the GlobalSoilMap project
(www.globalsoilmap.net). For many states, territories and nations, significant deficiencies may exist in
measured, accessible and available laboratory pH data. As a consequence, there is a potential role for
legacy pH observations over geographically widespread areas to complement available laboratory pH

data for digital soil mapping purposes (de Caritat et al. 2011; Hopley et al. 2014). The extensive
collections of field pH observations in state, territory and national government organisation databases
may also be valuable in establishing a baseline of soil condition where design-based monitoring systems
are absent.

At present, the documented pH datasets for field pH and lab pH measurements are large, but limited by the numerous confounding error sources that contribute to measurement uncertainty. Some of these unaccounted sources of uncertainty in field pH measurement include:

• assessor (experience level);

• pH test kits (different brands);

- soil characteristics (pH range and value);
- time-of-day (light quality), and
- age of test kit.
- 94

95 From practical field experience in conducting field pH measurements, there are many effects that could 96 potentially bias the relationship between lab pH and field pH. For example, it has been reported that 97 although Australian measurements of the spectral content of daylight have been similar to northern 98 hemisphere measurements, there is a higher level of irradiance in the ultraviolet spectral region (Dixon 99 1978). The effect on colour card matching and pH assessment over the course of the day is unknown 96 but there may be bias towards a higher pH reading.

Print quality of colour cards provided by different commercial field pH kits may introduce inaccuracy and uncertainty in pH test kits. The performance of indicator test kits can deteriorate over time due to solvents with aged dyes or impurities (Mason and Obenshain 1939). Also, batch-to-batch variations in the kit indicators and solvents may introduce perceptible shifts in performance. Very little research has been reported on these effects or on the potential impact of colour interpretation in the field.

106 The aim of this study is to address this gap in knowledge on sources of uncertainty affecting soil pH 107 determination by investigating how those factors may affect the relationship between field and lab pH 108 and quantifying the potential bias introduced by each factor. Two experiments to account for error

109	sources in both field and laboratory pH using Linear Models and the Maximum Likelihood Functional
110	Relationship (MLFR) as proposed by Ripley and Thomson (1987) were designed to test the following
111	hypotheses:
112	1. there is a significant assessor effect on the analytical bias between field and lab pH;
113	2. there is a significant pH level effect, and
114	3. there is a significant test kit effect.
115	
116	The effect of light quality was considered as time-of-day and has been used as a blocking factor in this
117	study. The findings from these experiments will provide support for recommendation of a more "robust"
118	measurement methodology of field pH in future applications such as soil surveys and contribute to the
119	harmonization of existing legacy field pH datasets with laboratory pH data used in digital soil mapping
120	and monitoring applications.
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133 presented in Table 1.

134 Laboratory analysis for the experiments was undertaken in triplicate to estimate error in laboratory measurement. Measurements were determined using a Radiometer Analytical (Lyon, France) titration 135 system comprising PHM92 pH meter, CDM240 conductivity meter and SAC950 sample changer. The 136 instrument was calibrated according to the manufacturer's specifications with a reported laboratory 137 138 precision of $<\pm 0.1$ pH units. Initial pH_w results were from numerous batches, and as a consequence there is greater batch-to-batch variability in these results in comparison with the second and third 139 140 measurement that were obtained in the single batch. All batches included two control samples, as 141 recommended, to account for instrument drift (Laslett and MacBratney 1990).

142

143 Psychophysical assessment of field pH

Experimental assessment of field pH using the pH test kit followed the standard protocol for a 144 145 psychophysical experiment involving human perceptual judgements recorded on a psychometric scale 146 (Benke et al. 1988). Psychophysical measures were in the form of colour assessments using a colour 147 card with 16-step scale for matching colour against treated soil samples for field pH determination. To 148 compare and contrast regular users of the field pH kit such as trained pedologists involved in soil and 149 land survey (Experienced group) against those that may have used a kit irregularly or not at all (Inexperienced group), two groups of assessors (Assessor Type) were selected based on their test results 150 151 from an online colour-blind test called the Farnsworth-Munsell 100 Hue Colour Vision Test (Farnsworth 1943). The ten subjects were male and female technical and scientific staff volunteers. All 152 153 subjects had 20/20 vision wearing their normal correction. Ages of subjects ranged from 35 to 60 years. 154 Each subject carried out three colour assessment sessions (two on the first day at Early and Late afternoon and one on the second day at noon). 155

156

157 Field pH test kits

Two commercially available soil pH test kits were used in this study (referred to as Kit 1 and Kit 2) and were based on the Raupach and Tucker (1959) field pH determination procedure. Both kits used the same assessment procedure where a soil sample (<1 teaspoon) was mixed with the indicator solution until a thick paste was established. The paste is then dusted with BaSO₄ (barium sulphate) powder (used as an optical enhancing agent) and the colour assessed against the colour card after 1 to 2 minutes to find a nearest match.

164

165 *Time-of-day (light quality)*

One of the major influencing factors in colour differentiation is light quality (or lack of it) which reflects the background environmental lighting, glare from the light source and veiling reflection. This is directly influenced by the time-of-day for measurement of field pH. Time-of-day, in the remainder of this paper, will be used interchangeably with light quality. Since time could not be randomised, it was fixed as a blocking factor with two classes: 1PM and 5PM.

171 It was decided that early and late afternoon (Period) would be good surrogates for good and poor quality
172 light respectively. Both experiments were conducted outside in April 2015 on sunny days with clear
173 blue skies.

174

176 Two experiments were conducted to test hypotheses 1 and 2 (Experiment 1) and hypothesis 3177 (Experiment 2).

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179 Experiment 1
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At each time period, samples were randomly allocated to the 10 assessors for field pH assessment. Each
participant was randomly allocated samples of the 13 pH levelsto detect if any significant difference in

¹⁷⁵ Experimental design

182 colour differentiation between assessors exists and if differentiation is consistent across the full183 spectrum of colours (or pH levels). This was phase A of Experiment 1.

Phase B of this experiment involved each assessor completing pH assessments in triplicate on at least 3 pH levels (for example, Assessor 1 might be allocated pH levels 4.0, 6.5 and 9.5 and Assessor 2 might receive pH levels, 4.5, 6.0 and 10, etc). One assessor in each group (Experienced or Inexperienced) assessed pH levels on four samples to complete the set of measurement errors for each of the pH levels*Assessor Type. This data was combined with the triplicate lab pH data to provide measurement error estimates on both field pH and lab pH enabling an assessment of potential bias by fitting models that accommodate for errors in both field and lab pH.

The above two phases (A and B) were combined into one single experiment in a full factorial of Assessor*pH level in a randomised complete block design (RCBD), where time-of-day were used to group pH assessments as the blocking factor. Phase B was incorporated using the same design but with an extra randomisation of Assessor to pH level for conducting triplicate field pH measurements. The same randomisation was fixed for 1PM and 5PM for practical reasons, that is, Assessor and pH level pairing were consistent and an extra replication for a better estimate of the Assessor consistency.

197

198 Experiment 2

In this experiment, Kit Type, Assessor (and Assessor Type) and pH level were included in a split-plot
design where Assessor was used as a blocking factor, pH level was the whole-plot factor and Kit Type
was the sub-plot factor respectively.

202

203 Statistical analyses

204

205 Exploratory analyses

Trellis plots were used to plot data from both experiments in order to explore any potential relationship between variables as a basis to inform further formal statistical modelling. In Experiment 1 (phase A), field pH was plotted against lab pH in panels (Figure 2), where each trellis/panel represented each Assessor (A-J). In the same experiment, field pH was again plotted against lab pH in panels, but this time each trellis/panel represented Assessor Type (Experienced and Inexperienced).

In Experiment 2, field pH was again plotted against lab pH in panels, but this time the panels were extended to include a double layer of Assessor and Kit Type where each panel represented a combination of those two factors.

All plots were constructed using the lattice 0.20-31 package (Sarkar 2008) in R and implementing modified codes to accommodate our data structure and visual display requirements. All plots were performed in the R statistical software (R Development Core Team 2015).

217

218 Formal analyses

To compare the performance of Assessors in Experiment 1 (phase A) and Kit Type in Experiment 2, a relevant measure was necessary to compare how well an assessor managed to measure the field pH of their allocated samples. The closer the field pH values are to the lab pH values, the higher the precision of the Assessor or Kit Type in determining pH value. An absolute difference between field pH and lab pH was used as the variable of interest.

In Experiment 1 (phase A), the absolute difference was analysed using Analysis of Variance (ANOVA). The treatment structure was specified with fully factorial effects for Assessor Types in full factorial combination with Level (pH levels). The treatment structure was set as Assessor Type* pH level, the blocking structure was specified as Samples nested within Assessor and nested within Period (Period/Assessor/Sample).

To detect potential bias between lab pH and field pH, an estimated measurement error for both methods(field method and lab method) was produced in Experiment 1, phase B. Given that triplicate samples

were allocated to both the Experienced and Inexperienced groups on both experimental periods (Early
and Late afternoon), it is possible to look at the potential bias for all combinations and of Assessor
Type*Period as well as a combined data (ignoring the groups).

Given that data were available for all combinations of time-of-day and Assessor Type, four scenarios
were tested: 1. Experienced and 1PM; 2. Experienced and 5PM; 3. Inexperienced and 1PM; and 4.
Inexperienced and 5PM. For each combination and the combined data, two models for field pH and lab
pH were fitted: Linear Model (LM) and the Maximum Likelihood Functional Relationship (MLFR).
Both models were adapted to test (1) if the intercepts were significantly different from 0, and (2) if the
slopes were significantly different from 1, both of which formed the basis for our bias detection.

In Experiment 2, the absolute difference between test kits was analysed using an ANOVA appropriate for a split-plot design. The treatment structure was specified with fully factorial effects for Kit Type in full factorial combination with pH level. This was coded in GenStat as Kit Type*pH level. Assessor was specified as the blocking structure. Residual diagnostics performed in the analysis of Experiment 1 (phase A) were similarly performed here.

In all the ANOVA analyses (for Experiment 1 and 2), residual values were examined graphically to check for distributional normality and constant variance assumptions. Observations with standardised residuals greater than 3.0 were excluded from the analyses. The absolute difference data was square root transformed during analysis to establish normal distribution and constant variance. Least significant differences (5% level) were used to separate the means, subject to significant F-tests.

ANOVA analyses in Experiment 1 (phase A) and Experiment 2 were performed using the GenStat® statistical package (GenStat® Release 16.1, Copyright 2013, VSN International Ltd). The LM model was fitted using modified code based on a built-in LM function. The MLFR function was written based on the methodology described in Ripley and Thomson (1987). Both functions were implemented using the R statistical package (R Development Core Team 2015).

255

256 Results

257 Experiment 1

A trellis plot of lab pH versus field pH is shown below in Figure 2. Each panel from A-J represents the information for each Assessor. In each panel, lab pH (x-axis) is plotted against field pH (y-axis) with least-squares lines fitted to the data. The fitted model is plotted against the 1:1 line (in red) with slope=1 and intercept=0 for comparison. The estimates for intercept and slope of the LM are printed in each panel, along with the estimated R^2 . Each Assessor produced a different fit for the least-squares model with different intercept and slope estimates. This implies that there were different abilities between assessors to determine pH measurements in the field using a specific field pH kit.

A trellis plot of lab pH versus field pH (Figure 3), where the trellis is either Experienced (Yes) or Inexperienced (No), suggests that the two groups are different. The slope, intercept parameter and estimated R^2 were all different. This implies that a significant difference exists between the experienced and inexperienced Assessors in their ability to conduct soil pH measurements.

The ANOVA results showed that the main effects of Type (P<0.05) and pH Level (P<0.001) were significant but the interaction was not (Table 2). This implies that experienced Assessors were able to more accurately determine pH than inexperienced Assessors. The magnitude of error (getting the pH wrong) varied with pH level. It appeared that the degree of difficulties varies from one pH level to the next and this was consistent for all Assessors.

274 In phase B of Experiment 1, mean pH and corresponding measurement errors for all the samples using 275 a laboratory pH meter and standard field technique (pH kit) were averaged over all four groups then 276 modelled using the MLFR and LM functions in R. Summary statistics are provided in Table 3. For the LM, the intercept or α (1.214) is significantly (P<0.05) different from 0; the slope or β (0.8064) is also 277 278 significantly (P<0.01) different from 1, signifying that there was a bias between lab pH and field pH in 279 both the intercept and the slope. For MLFR, the intercept ($\alpha = 0.342$) was marginally (P<0.1) different from 0 and slope ($\beta = 0.9341$) was significantly (P<0.05) different from 1. The MLFR result is much 280 281 more conservative than the LM as the standard error of the parameter ($\alpha = 0.182$ and standard error for 282 β (0.0269) are tighter (better estimated). However, both methods (MLFR and LM) showed that there

was a bias between lab pH and field pH. Figure 4 below shows that the LM (red line) and MLFR (green
line) deviates from the 1:1 line (black). Both reveal bias with the LM biased at both extremes, whereas
MLFR is biased at the high end only (indicating pH is more alkaline).

In the following analysis, all samples were split based on the combination of Assessor Type by time-286 of-day. The results of each combination are summarised in Table 4 and Figure 5. In Table 4, only 287 288 statistics for the MLFR fit are presented as they are more robust. The MLFR parameter fits for the four 289 scenarios of Assessor Type and Light quality showed that the slope and intercept parameters were biased. The LM fits are still shown in Figure 5 for comparison. Experienced assessors were positively 290 biased at 1PM ($\alpha = 0.7572$) and 5PM ($\alpha = 0.3477$) with intercepts significantly different from 0 at 291 P<0.01. Inexperienced assessors were also biased at 1PM ($\beta = 1.5476$) and 5 PM ($\beta = 1.4273$) with 292 293 slopes also significantly different from 1 at P<0.01.

294

295 *Experiment 2*

Two trellis plots are presented including field pH versus lab pH by Kit Type and Assessors (Figure 6), and field pH versus lab pH by Kit Type and Assessor Type (Figure 7). Each panel represents the information for each Assessor by Kit. The parameter (α and β) estimates for each panel are different, indicating a significant effect of Kit and Assessor (experience) on the bias between field pH and lab pH. The Assessor is the same as the panels in Figure 2.

Figure 6 showed that almost all fitted linear models were below the 1:1 line in the panels, indicating 301 302 that field pH (measured by assessors) were almost always underestimating the lab pH (assumed to be 303 the true pH) and this was consistent for all assessors regardless of experience. For each Assessor, it is 304 possible to compare between Kits using the paired panels. For example, panel 1 (Assessor A using Kit 1) can be compared with panel 2 (Assessor A using Kit 2). Similarly, panel 3 and 4 can be used to 305 compare Assessor B using Kit 1 and 2 and so on. For each Assessor, a comparison between the fitted 306 linear models to the 1:1 lines by Kit 1 and Kit 2 can be used to determine any potential difference 307 between Assessors, Kits and their interactions. From this, we obtain the following summary: 308

309	• As	sessor A: performed better using Kit 2;
310	• As	sessor B: no difference;
311	• As	sessor C: no difference;
312	• As	sessor D: performed better using Kit 2;
313	• As	sessor F: performed better using Kit 2;
314	• As	sessor G: performed better using Kit 2;
315	• As	sessor H: no difference;
316	• As	sessor I: no difference, and
317	• As	sessor J: performed better using Kit 2.

In Figure 7 we can compare Kit 1 versus Kit 2 as well as Experienced (Yes) versus Inexperienced (No). Looking at all four panels, there was a difference between Kit 1 and Kit 2 where Kit 2 produced results that were closer to the lab results. This was consistent, regardless of the assessors' experience. Both Figures 6 and 7 indicate that there might be a significant difference between Kit and Assessor but no significant interaction between Assessor and Kit.

The ANOVA results (Table 5) identified that the main effects of Kit type (P<0.001) and pH Level (P<0.01) were significant but the interaction was not. The Kit type effect implied that using Kit 2, the assessors were able to obtain more accurate pH measurements than using Kit 1. The magnitude of error (getting the pH wrong) varied with pH levels as in Experiment 1. The degree of difficulties varied from one pH level to the next and this was consistent for both kits (on the whole).

329

- 330 **Discussion**
- 331 Assessor experience

This study confirms that pH measured in the field has many potential sources of error, one of which isthe experience of the user (Assessor). The experiments highlight that inexperienced field pH assessors

334 under-perform against experienced assessors, and therefore a greater uncertainty, bias and error with field pH assessments can be expected from inexperienced assessors. This would suggest that for users 335 with limited, or no previous experience using a field pH kit, there is likely to be greater error in the pH 336 determination and therefore greater caution required when using these measurements for decision 337 338 making, e.g. lime application. This does not account for spatial or temporal variability which are additional sources of uncertainty besides measurement error and epistemic error sources explored in the 339 340 experimental design. From Experiment 1 to Experiment 2, there is the potential for those with limited 341 to no experience to learn from others that participated in earlier assessments. This is akin to on-the-job 342 training where junior or 'inexperienced' surveyors learn the field determination method under the 343 guidance of an experienced operator with field pH determination. These findings suggest that 344 introductory training and guidance from experienced users in the application of a field pH kit can be 345 extremely beneficial to achieve accuracy and precision in pH determinations. Ongoing quality 346 assurance and control should also be considered as part of regular testing regimes for persons measuring field pH. 347

While differences between the two assessor groups were evident, there was no clear relationship between the pH level of assessment and the assessor group across the pH range of this study. There were pH levels that were more difficult to assess than others such as pH levels 6.5 and 10. The experiment reveals that the differences in performance are most likely due to the interpretation of the colour card at these pH values rather than the quality or age of the indicator solution or barium sulphate.

353 There are difficulties in interpretation of the colour graduation on the cards, especially for males which 354 have a deficiency in the red/green region (as evident in results from the Ishihara colour chart). In 355 collated soil site information from soil and land surveys in Victoria contained in the VSIS, there are 51 356 reported surveyors that have participated in studies where field pH observations have been collected for 357 3398 sites. Of the 51 surveyors, only 20% are female. It is unclear how many of the surveyors were 358 properly assessed for vision impairment or were adequately trained for field pH determination, 359 although, often in the field surveyors would cross-reference with one another especially if uncertain on 360 the pH assignment class.

362 Model and bias

363 All participants in this study demonstrated different abilities to predict pH using the field determination method. This was reflected in the different bias, error and model fit for every assessor. As there is bias 364 365 represented in the LM and MLFR models between field pH and lab pH, there is a need for users of such 366 assessments to be prudent as field pH results in this study do not agree perfectly with pH data measured 367 in the laboratory. While both the LM and MLFR display a bias between lab pH and field pH, the MLFR 368 provides a much improved fit than the LM which is biased at both high and low pH values, whereas the 369 MLFR is biased only for high pH values. Further improvements of the MLFR over the LM are evident 370 where the standard error of the model parameters is considerably less than those of the LM.

371 Baker et al. (1983) and Steinhardt and Mengel (1981) have established quite different results for bias 372 in the relationship between field and laboratory pH measurements. This study also achieved systematic 373 differences (bias) for the different assessors and assessor groups. Strong agreement between field pH 374 and lab pH has been found where one experienced assessor completes all field pH assessments (Baker 375 et al. 1983). From our study the samples were specifically chosen to represent the spread of pH levels 376 represented in the colour cards, but also variations in soil properties such as colour, depth, clay % and 377 organic carbon content that may contribute to error in measurement. This provides a degree of confidence in the agreement between methods being maintained for a significantly larger sample size. 378 379 It is unclear, and beyond the scope of this evaluation, if soil colour made a difference to perception of 380 pH level.

381

382 *Time-of-day (light quality)*

Another potential source of uncertainty in field determination of pH is the quality of light. Although this study did not formally test light quality, as we were unable to randomise time in our experimental design, we did assess, using a LM and MLFR, if there were differences between two different times of 386 day that were intended to represent good quality and poor quality light. The results demonstrated that with measurement errors for both the lab pH and field pH, we were able to detect bias in the slopes and 387 intercepts for the four scenarios of time-of-day and assessor group. The MLFR model for the 388 experienced assessor group was better than the inexperienced for 1PM and 5PM. Observation time was 389 390 not a significant factor for both experienced and inexperienced assessor groups. This is not surprising given that light quality (brightness and glare) for the two times of day of the experiment (1PM and 391 392 5PM) was relatively similar. Glare as a light quality factor was noted as an issue in pH assessment by 393 assessors of both groups. On the first day (Experiment 1), the light quality at 5PM was considered as 394 good, if not better than the light quality at 1PM. In our pre-experiment design, we had expected that light quality later in the day would be poorer, but this effect was not observed. It is expected that light 395 396 quality will be a significant factor for both experienced and inexperienced assessors in future experiments, if we can replicate and quantify true "good" and "poor" light quality in our design. 397

398

399 *Kit type differences*

400 A final source of uncertainty considered in this study was difference between commercially available field colorimetric indicator pH kits. Both kits used in this study resulted in underestimated lab pH for 401 all assessors. There were consistently better results achieved for all assessors regardless of experience 402 403 for Kit 2 in comparison with Kit 1. The pH levels differences between the kits were inconsistent 404 although there were some pH levels (e.g. 7.5) that had an absolute difference between the two kits close 405 to 1. This could potentially be due to a number of error sources including indictor and BaSO₄ impurities 406 or slight differences that were apparent in the colour cards for the two kits. This requires further 407 investigation as users of field pH kits need confidence in the ability to easily contrast the treated sample 408 with colours represented on the indicator card.

The comparison of kits has highlighted that it is prudent to remove kit type error as a potential source and use one kit type only. Batch to batch variation in kits is potentially a substantial source of error, especially where impurities exist in solvents and reagents, but this was not able to be factored into the experimental design for this study.

414 General comments

Field pH measurements have been used for soil survey and agricultural advisory work for over 60 years, 415 highlighting the robustness, simplicity and reliability of the procedure. Field determination of soil pH 416 417 using the Raupach and Tucker (1959) procedure can produce reliable results in comparison to laboratory pH. In particular, field pH determination has provided a role in the screening of samples for potential 418 419 laboratory analysis, should it be required. A benefit of the current field pH method is that there has been 420 no change to the methodology and chemical constituents since its conception. In contrast, modifications to laboratory techniques over the last 60-years including stirring effects and operator differences are 421 422 likely to represent sources of uncertainty in legacy pH data greater than currently reported values, e.g. 423 ± 0.1 pH unit. This suggests that as a method for determining soil reaction, it has been an adequate 424 servant for many soil mapping activities over this period.

In the absence of representative laboratory measurements, there is little evidence to suspect that field determinations with greater uncertainty cannot serve as useful replacements for laboratory measurements in spatial and temporal assessments for mapping and monitoring purposes. The findings from this study support the wider use of legacy field pH data for soil mapping purposes at regional to national scales. A mapping technique that could utilise legacy field pH observations in partnership with lab pH is a linear model of coregionalization (LMCR; Webster and Oliver 2001) using a model-thencalculate, or, calculate-then-model approach described by Orton et al. (2014).

432 The two experiments reported in this study provide an account of error sources that add to field pH uncertainty. By understanding the nature and magnitude of these errors, we can determine and 433 434 understand the error bounds represented by the confidence and prediction intervals and provide information on error propagation in mapping and modelling applications. Further investigation to 435 understand the errors in soil survey should be considered to screen legacy soil pH observations prior to 436 use in regional monitoring or mapping applications. The differences found between experienced and 437 inexperienced operators of field pH kits can also be used to guide cleansing of field pH from various 438 439 sources, such as data from citizen science and crowd sourcing (Rossiter et al. 2015).

440 Other factors unaccounted for in explaining differences between field and laboratory pH include 441 oxidation effects due to soil storage conditions (Slattery and Burnett 1992) and incorporation of 442 pedogenic segregations (e.g. calcareous) into the <2mm fraction through differences in sample 443 preparation procedures.

444 While dealing with legacy data can be problematic due to insufficient metadata to isolate effects due to operator experience, test kit differences and light quality characteristics at time of observation, this 445 446 should not preclude the capture of new error sources in future. Practical suggestions to increase the 447 certainty in field pH data include: a level of training to provide assessor certification across the soil pH 448 range; field kits should be regularly tested against known standards, and the test kit should be identified 449 in metadata associated with field measurements. Also to be noted are date and time of observation 450 recorded, and assessor and other factors that may contribute to potential significant differences between 451 field and laboratory measurements (e.g. soil moisture status, observed segregations, depth).

452 An important consideration when assessing pH in the field or laboratory, or producing maps for planning and land use decision-making, is what is the intended use or purpose of the data. While high 453 454 precision and accuracy is generally useful, it is often the critical pH ranges relevant to management 455 (e.g. effect plant production, nitrate leaching into groundwater and waterways or corrosion of 456 infrastructure) that are sought. Using the diagnostic pH ranges described by Slattery et al. (1999) as a 457 guide, the critical range of 5.3 to 5.8 is where accurate measurements are most valuable due to the sensitivity of grain and pasture cultivars from the effects of exchangeable manganese and aluminium at 458 459 these levels. Below this threshold there are implicit and known significant impacts to plant production where remediation actions are necessary. But is high accuracy and precision required here? Likewise, 460 above a pH of 5.8, there are few limitations except where trace elements such as zinc and molybdenum 461 are less available to plants at pH values of 8 and above. Unpublished investigations by the authors 462 463 identify interquartile range (IQR) values for field pH values 5, 5.5 and 6 against laboratory measurement as 4.9-5.5, 5.1-5.6 and 5.4-6.1. These IQRs suggest that field pH determinations around this diagnostic 464 range are more than just useful indicators especially given that the amount of agricultural land to have 465 466 pH values in this pH range or below was expected to double to 43-64 million hectares in the coming 467 decade (Dolling et al. 2001).

469 Conclusion

470 Field pH is a useful indicator of soil condition and has practical value for soil pre-screening and rapid classification. Field observations may have additional utility in soil mapping where there is insufficient 471 data available from laboratory pH determinations. While field pH determinations are not as accurate as 472 laboratory measurements, they do provide valuable support for laboratory measurements that are 473 474 spatially and temporally sparse or biased. This evaluation study of field pH test kits has demonstrated 475 that user experience with a pH test kit will have an impact on the prediction accuracy and uncertainty. 476 This study also confirmed that sources of uncertainty in field pH assessments, such as choice of kit, will 477 affect the accuracy and bias of pH determination in comparison to laboratory measurements.

478 Using the field colorimetric method, some pH levels at the extreme range were more difficult to 479 determine than others, regardless of assessor experience. There is likely to be bias between field and 480 laboratory measurements and there are distinct benefits from using a kit free from impurities and with a colour card that is consistent with colours expressed in treated samples. Mixing of commercial kits 481 482 when attempting to harmonise legacy measurements because of differences between the kits may introduce additional uncertainty. The experimental methodology implemented for this study could be 483 modified to accommodate further test subjects and potential error sources, such as within-kit and 484 485 between-kit variability, or to consider spatial and temporal variability as additional factors. It is 486 recommended that further investigation is pursued on the possible effects of sample size and gender on 487 test kit performance and reliability.

488

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2 Figure 1 Samples used in experiments with pH level





5 Figure 2 Trellis plot of field pH versus lab pH by Assessor. The red dashed line is the 1:1 line.



10 Figure 3 Trellis plot of field pH versus lab pH by Experience. The red dashed line is the 1:1 line.



Figure 4 Field pH versus lab pH with fitted models using LM (black line) and MLFR (blue line). The
 red dashed line is the 1:1 line.



17

18 Figure 5 Field pH versus lab pH for the four different scenarios - (Case 1) Experienced and 1PM (top

- left-hand corner), (Case 2) Experienced and 5PM (top right-hand corner), (3) Inexperienced and 1PM
 (bottom left-hand corner) and (4) Inexperienced and 5PM (bottom right-hand corner). The black line
- 21 is the 1:1 line.
- 22



Figure 6 Trellis plots of field pH versus lab pH by Kit by Assessor.



28 Figure 7 Trellis plot of field pH versus lab pH for Kit by Assessor Type.

Site	ASC	Depth	Clay % ¹	E.C. $(dS/m)^2$	Org. C % ³
	(Isbell	(cm)			
	2002)				
USFS_VP100	CH	10-20	33	0.06	1.65
USFS_VP11	SO	0-10	21	0.10	2.30
USFS_VP32	SO	0-10	23	0.15	2.97
USFS_VP36	CH	80-90	51	0.18	0.55
USFS_VP38	SO	40-50	49	0.17	0.74
USFS_VP5	CH	90-100	86	0.13	0.37
USFS_VP66	CH	0-10	22	0.12	2.78
USFS_VP71	CH	90-100	34	0.09	0.38
USFS_VW150	CA	60-70	53	2.43	0.28
USFS_VW55	CA	80-90	28	0.72	0.53
CSMP_89_C1	DE	38-75	41	0.26	10.05
CSMP_100_C1	VE	69-92	34	0.87	3.07
SW22	DE	5-25	10	0.14	9.60

Table 1 Site, sampled depth, ASC order and soil properties

 ¹ From laboratory or Mid-Infra-Red (MIR) prediction
 ² Method 3A1 from Rayment and Lyons (2011)
 ³ Method 6B3 or 6B4 from Rayment and Lyons (2011) 32 33

36	Table 2 ANOVA for the absolute difference between lab pH and field pH with two types of assessors
37	and thirteen levels of pH. Mean values (back-transformed mean) are presented.

Factor	Absolute difference	
Type of Assessors		
Experienced	0.75 (0.56)	
Inexperienced	0.90 (0.81)	
LSD(5%)	0.14	
pH Levels		
4.5	0.61	
5.0	0.83	
5.5	0.73	
5.5	0.85	
6.0	0.85	
6.5	1.08	
7.0	0.80	
7.5	0.88	
8.0	0.86	
8.5	0.77	
9.0	0.70	
9.5	0.66	
10.0	1.12	
LSD(5%)	0.24	
F-test probabilities		
Types of Assessor (T)	0.03	
pH Levels (L)	<0.001	

40 Table 3 Summary of LM and MLFR model parameters between pH data measured in the field (from

41 our experiment) as the response variable (y) and pH data measured in the laboratory as the fixed

42 variable (x).

	LM	MLFR
Intercept (a)	1.2137	0.3424
Standard error of Intercept (s.e(α))	0.5156	0.1820
Probability $\alpha \neq 0$	0.0186	0.0599
Slope (β)	0.8064	0.9341
Standard error of Intercept (s.e(β))	0.0695	0.0269
Probability $\beta \neq 1$	0.0053	0.0142

43

45 Table 4 Summary of MLFR model parameters for field pH (y) and lab pH data (x) for four scenarios:

46 (Case 1) Experienced and 1PM, (Case 2) Experienced and 5PM, (3) Inexperienced and 1PM and (4)

47 Inexperienced and 5PM.

	Case 1	Case 2	Case 3	Case 4
Intercept (a)	0.7572	0.3477	1.5476	1.4273
Standard error of Intercept (s.e(α))	0.3393	0.2381	0.5273	0.4933
Probability $\alpha \neq 0$	0.0257	0.1443	0.0033	0.0038
Slope (β)	0.8705	0.9178	0.8256	0.8315
Standard error of Intercept (s.e(β))	0.0430	0.0347	0.0604	0.0580
Probability $\beta \neq 1$	0.0026	0.0177	0.0039	0.0037

48

Factor	Absolute difference	
Kit Type		
Kit 1	0.603	
Kit 2	0.473	
LSD(5%)	0.0924	
pH Levels		
4.5	0.372	
5.0	0.357	
5.5	0.411	
5.5	0.481	
6.0	0.506	
6.5	0.602	
7.0	0.653	
7.5	0.919	
8.0	0.681	
8.5	0.602	
9.0	0.452	
9.5	0.473	
LSD(5%)	0.2532	
F-test probabilities		
Types of Kits (K)	0.006	
pH Levels (L)	< 0.001	

50 Table 5 ANOVA for the absolute difference between lab pH and field pH with two kits and twelve

⁵¹ levels of pH. Mean values are presented.

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Site	ASC	Depth	Clay % ¹	E.C. $(dS/m)^2$	Org. C $\%^3$	
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