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1 Estimation of Soil Clay Content from Hygroscopic Water Content Measurements

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24

25 **ABSTRACT**

26 Soil texture and the soil water characteristic (SWC) are key properties used to estimate
27 flow and transport parameters. Determination of clay content is therefore critical for
28 understanding of plot scale soil heterogeneity. With increasing interest in proximal soil sensing,
29 there is the need to relate obtained signals to soil properties of interest. Inference of soil texture,
30 especially clay mineral content, from instrument response from electromagnetic induction and
31 radiometric methods is of substantial interest. However, the cost of soil sampling and analysis
32 required to link proximal measurements and soil properties, e.g. clay mineral content, can
33 sometimes outweigh the benefits of using a fast proximal technique. In this paper, we propose
34 that determination of a soil's hygroscopic water content at 50% atmospheric relative humidity
35 (RH^{50}), which is time and cost efficient, and particularly suitable for developing countries, can
36 act as a useful surrogate for clay content in interpreting soil spatial patterns based on proximal
37 signals. We used standard clays such as kaolinite, illite and montmorillonite to determine the
38 water release characteristic as a function of hygroscopic water content. We also determined clay
39 content of soils from temperate (Arizona, USA) and tropical (Trinidad) regions using the
40 hydrometer method, and hygroscopic water content for soils equilibrated at RH^{50} . We found
41 linear dependence of clay percentage and RH^{50} for a range of soil mineralogies. Hygroscopic
42 water measurements offer an inexpensive and simple way to estimate site specific clay mineral
43 content that in turn can be used to interpret geophysical signal data in reconnaissance surveys.

44

45 **Keywords:** Hygroscopic water, clay, water release curve, soil texture, geophysics, radiometrics,
46 electromagnetic induction

47 **Abbreviations:** EMI, electromagnetic induction; RH, relative humidity; SWC, soil water
48 characteristic.
49

50 INTRODUCTION

51 Soil texture (percentage of sand, silt and clay) is a fundamental parameter in soil science
52 (Gee and Bauder, 1986) and a major component of the soil natural capital (Robinson et al.,
53 2009a). Texture is widely used in agriculture and engineering as well as in basic research to
54 estimate for example water release curves in flow and transport modeling (Schaap et al., 2001).
55 Soil texture, especially clay content, controls magnitude and rates of many physical, chemical
56 and hydrological processes in soils. Important soil phenomena such as nutrient storage, nutrient
57 availability, water retention, and stability of aggregates may vary across the field in response to
58 the spatial variability of clay percentage. Soil moisture which is the major control for rainfall-
59 runoff response in a watershed (Robinson et al., 2008a) has been directly linked to clay
60 variability (Crave and Gascuel-Oudou, 1997). Net nitrification and CO₂ release has been shown
61 to depend on water content and clay content (Schjonning et al., 2003). Knowledge of texture,
62 especially the spatial distribution of clay content, is therefore important for a range of ecosystem
63 services, including provisioning through agricultural production and regulating of the
64 hydrological cycle through filtering and buffering. A growing challenge in soil science is to map
65 soil natural capital, of which texture is a component, in a way that allows us to scale from the
66 soil profile, to field, to regions.

67 Proximal sensing techniques, especially geophysical sensors that infer spatial textural
68 information from instrument response to ions adsorbed on clay minerals (Robinson et al.,
69 2008b), provide an invaluable means for filling the ‘intermediate’ scale data gap.
70 Electromagnetic induction (Doolittle et al., 1994; Triantafilis et al., 2001; Triantafilis and Lesch,
71 2005), resistivity (Samouelian et al., 2005), induced polarization (Slater et al., 2006) and
72 radiometrics (Rawlins et al., 2007) are techniques progressively used to determine soil properties

73 or spatial patterns related to texture, inferred from mineralogy and cation binding. In case of
74 electrical methods, cations adsorbed to 2:1 clay minerals can be used to interpret, or determine,
75 the spatial pattern of clay percentage in non-saline soils (Triantafilis et al., 2001; Triantafilis and
76 Lesch, 2005; Sudduth et al., 2005; Harvey and Morgan, 2008). This method is limited to clays
77 that adsorb cations to counter balance negative charge sites, and is less likely to work for clay
78 minerals with low surface areas, e.g. kaolinites. In case of radiometrics, many clay minerals e.g.
79 hydrous micas and illites can be detected through their potassium isotope signal (Taylor et al.,
80 2002). Knowledge of clay content is therefore critical for the signal interpretation of proximal
81 sensing instruments.

82 Direct, grid-like soil sampling for identifying spatial textural patterns has several
83 limitations among which the need for high-intensity sampling and associated costs for analyses
84 are the most constraining ones. In addition, minimizing soil disturbance, i.e. not filling the
85 landscape with holes is vital for many hydrological process studies. In many cases, an
86 understanding of soil spatial patterns, and delimiting of hydrological functional units, is more
87 important than the exact knowledge of soil properties (Grayson and Blöschl, 2000). The costs for
88 independently measuring soil properties for calibration of proximal signals have always been an
89 issue, such that Lesch et al. (1995 a, b) developed efficient sampling methods for interpreting
90 EMI signal response from directed soil sampling. Even with approaches like theirs, the particle
91 size analysis presents a substantial cost for calibration, especially if multiple fields are sampled.

92 In this paper we propose that under many circumstances, a site specific calibration
93 between clay percentage and hygroscopic water content could be used to greatly reduce the
94 number of particle size analyses that might be done for a proximal sensing site calibration.
95 Estimating clay percentage from hygroscopic water content presents a cost efficient, simple and

96 reliable surrogate for correlating proximal signal response to soil clay content; although the
97 paper does not specifically explore EMI calibration. Our major goal is to investigate if simple,
98 cost and time efficient hygroscopic water content measurements can be used to estimate clay
99 contents for soils with varying mineralogies.

100 In soils, soil solution electrical conductivity EC_e , volumetric soil water θ_v and clay
101 contents are the major factors influencing bulk soil electrical conductivity EC_a (Friedman, 2005)
102 and EMI signal response. In the case of radiometrics, clay content, and to a lesser extent soil
103 moisture are the driving factors. The intimate relationship between soil clay content and
104 hygroscopic water content is well established (Briggs and Shantz, 1912, Banin and Amiel, 1970;
105 Petersen et al., 1996), but not widely exploited. It was proposed as a method for determining soil
106 surface area, but largely abandoned because water tends to cluster on charged clay mineral
107 surfaces, not forming a monolayer like EGME, which has a lower dielectric constant, or non-
108 polar nitrogen (Quirk and Murray, 1999). Therefore, we hypothesize that soil hygroscopic water
109 content, whose determination is fast and technically less involved than particle size analysis,
110 positively correlates with clay percentage in both temperate and tropical soils, and can provide a
111 useful surrogate for soil clay content. Other research groups have presented results that
112 emphasize the strong correlation between hygroscopic water and clay contents (Banin and
113 Amiel, 1970; Petersen et al., 1996, Tuller and Or, 2005; Resurreccion et al., 2011), however,
114 there is no specific water potential or relative humidity agreed upon at which these relationships
115 should be determined.

116 Clay content and type of clay minerals determine the magnitude of the soil specific
117 surface area (Petersen et al., 1996). Banin and Amiel (1970) presented data with specific surface
118 area showing a strong linear dependence ($r^2=0.902$) to clay contents. In the studies of Banin and

119 Amiel (1970) and Dirksen and Dasberg (1993), hygroscopic water content had a strong linear
120 correlation ($r^2=0.936$) with soil specific surface area. Recently, Logsdon et al. (2010) determined
121 hygroscopic water content of soils in a vapor-tight container over distilled water at ~99 %
122 relative humidity and concluded that higher hygroscopic water content is associated with high
123 soil specific surface area. To come to an agreement about a specific relative humidity level at
124 which hygroscopic water content ought to be determined, in-depth knowledge of the water
125 release characteristics of different clay minerals is required. Therefore, the objectives of the
126 present study were to: (1) determine the water release characteristics for standard source clays;
127 (2) define a suitable relative humidity level for estimating clay content for the source clays; and
128 (3) examine the relationship between hygroscopic water content and clay content using the
129 defined relative humidity for soils with varying mineralogies from temperate and tropical
130 regions.

131

132 **MATERIALS AND METHODS**

133 **Clay Minerals**

134 Standard 100 % source clay minerals were used to determine the hygroscopic water
135 content as a function of relative humidity. The selected samples were the same as used in Lebron
136 et al. (2009) and included: Silver Hill illite from Montana (IMt-1) and Ca-montmorillonite from
137 Cheto, AZ (SAz-1) obtained from the Clay Mineral Society's Source Clay Repository; Wyoming
138 bentonite (Aqua Technologies of Wyoming, Casper); and kaolinite from the Lamar pit (Bath,
139 SC). The SAz-1 montmorillonite was saturated with Na, Ca or Mg to produce clay samples
140 saturated with a single ion (Goldberg and Glaubig, 1987).

141

142 **Soil Samples**

143 The first set of samples contained tropical soils from the University of the West Indies
144 soil sample collection in Trinidad. Trinidad is the southernmost of the Islands of the Lesser
145 Antilles in the Caribbean Sea and is situated 10°3'N 60°55'W and 10°50'N 61°55'W. The 23 soils
146 used for this study were collected from different locations across the island, representing a range
147 of soil types including kaolinitic, micaceous, and montmorillonitic soils (Table 1). In addition,
148 20 temperate soils from the University of Arizona Department of Soil, Water and Environmental
149 Sciences' source soil collection, again representing a wide range of mineralogies and clay
150 content were analyzed (Table 1).

151 Furthermore, a number of datasets originating from both Trinidad and the USA that were
152 previously used for EMI calibration were investigated. Soils from Trinidad were collected from
153 Guayaguayare, Moruga, Centeno and Woodland from locations identified via an EMI-directed
154 soil sampling method (Lesch et al., 2000). Data from the USA were obtained from the T.W.
155 Daniel Experimental Forest (TWDEF) in northern Utah and the Reynolds Mountain East
156 catchment within the Reynolds Creek Experimental Watershed in southwestern Idaho (Abdu et
157 al., 2008).

158

159 **Clay and Soil Sample Analysis**

160 The water release characteristics for the source clays were measured with a Dewpoint
161 Potentiometer (WP4-T, Decagon Devices, Inc., Pullman, WA, USA). The clay samples were
162 oven dried at 105°C and then left equilibrating with the ambient laboratory atmosphere at
163 controlled temperature (25°C) for several months. Once the humidity level of interest had been
164 reached and was stable for 2-3 days, samples were weighed with an analytical balance and the

165 soil water potential was determined with the WP4-T. Relative humidity was measured using a
166 humidity sensor (Thermo Hygro, Thermo-Fisher, Waltham, MA). In order to establish a range of
167 humidities this experiment lasted about 5 months. Soil water potential was converted to relative
168 humidity via the well-known Kelvin equation:

$$169 \quad \Psi_w = \frac{RT}{M_w} \ln \left(\frac{e}{e_0} \right) \quad (1)$$

170 where Ψ_w is soil water potential, R is the universal gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the
171 absolute temperature ($^{\circ}\text{K}$), ρ_w is the density of water (kg m^{-3}) and M_w is the molecular weight of
172 water (0.018 kg/mol). The ratio of e , the water vapor pressure, to e_0 , the saturation vapor
173 pressure, is the temperature-dependent relative humidity, which can be rewritten as:

$$174 \quad \text{RH} = \frac{e}{e_0} = \exp \left(\frac{M_w \Psi_w}{\rho_w R T} \right) \quad (2)$$

175 The soil samples originating from Trinidad were first oven-dried at 105°C and then equilibrated
176 with the ambient atmosphere of a temperature-controlled room (25°C) with a monitored relative
177 humidity (Thermo Hygro, Thermo-Fisher, Waltham, MA) of $\sim 50\%$. The steps developed to
178 measure hygroscopic water content (θ_{hw}) at RH^{50} are described below:

- 179
- 180 1. Weigh the sample containers using a four-decimal analytical balance (W_c).
 - 181 2. Weigh approximately 10 g of air-dried sample into the sample containers and place them in
182 the oven to dry at 105°C for 24 hours, weigh again directly from the oven before cooling, using
183 a thermal isolator to protect the balance ($W_{ovendry}$).

184 3. Allow the oven-dried samples to equilibrate to RH^{50} at ambient conditions in the laboratory.
185 Equilibration of our samples was achieved within 48 to 72 hours when RH was monitored using
186 a thermohygrometer sensor.

187 4. Measure the humidity, monitor over a 2 hours period, if 50 % is maintained reweigh the
188 equilibrated samples to determine the moisture gain (W_{RH50}).

189 5. The θ_{hw} at RH^{50} in the sample is calculated gravimetrically as:

190

$$191 \theta_{hw} = \frac{(W_{RH50} - W_c) - (W_{ovendry} - W_c)}{(W_{ovendry} - W_c)} \quad (3)$$

192

193 The samples from Arizona were equilibrated at 50 % humidity and 25 °C using a temperature
194 and humidity controlled environmental chamber (1007H Temperature/Humidity Chamber,
195 TestEquity, LLC, Moorpark, CA, USA). An additional experiment was conducted to determine
196 how fast soils re-adsorb water following oven-drying. To achieve this, oven-dried soil samples
197 were weighed and kept in the environmental chamber at 50 % relative humidity and 25 °C. The
198 soil samples were then weighed in 3 hour intervals to capture the initially highly dynamic change
199 in water content. The time interval was then stepwise increased to 6, 12, and 24 hours for a total
200 time period of 15 days. The clay content was determined with the hydrometer method (Gee and
201 Bauder, 1986). Organic matter was removed using hydrogen peroxide (35 % H_2O_2) and
202 dispersed using 5 %-sodium hexametaphosphate.

203

204

205

206

207 **RESULTS**

208 **Source Clay Samples**

209 Results for hygroscopic water content (θ_{hw}) as a function of relative humidity are
210 presented in Fig. 1. The data for 2:1 clay minerals show a substantial increase in θ_{hw} at low
211 humidities, a levelling off at RH values between about 50-60 % and then increasing water
212 content again at RH values above 80 %. Both the 2:1 clays montmorillonite and illite adsorbed
213 more than 0.05 m³ of water per gram of oven dry soil at RH values of ~50 %. However, kaolinite
214 didn't adsorb water until ~80 % humidity or higher.

215

216 **Determination of Hygroscopic Water Content at RH⁵⁰**

217 Based on results from the water release curves (Fig. 1) we adopted the RH⁵⁰ for
218 equilibrating our soils as a compromise value considering the range of mineralogies. This also
219 represents a relatively stable point at which the change of θ_{hw} with humidity is at a minimum;
220 RH⁵⁰ is also commonly attained in the laboratory meaning no special equipment is required to
221 equilibrate the soils at this humidity.

222

223 **Water Uptake and Equilibration of Samples at RH⁵⁰**

224 After adopting the RH⁵⁰ for equilibrating our soils, we determined the time for samples to
225 readsorb water in the lab following oven drying. The results of the rate at which water uptake
226 occur using the Arizona soils data set after oven drying is presented in Fig. 2. The facilities at the
227 laboratory in Arizona allowed samples to be analyzed in greater detail under more tightly
228 controlled conditions. In our experimental method soils are oven dried and then allowed to re-
229 equilibrate at RH⁵⁰ to determine the fraction of hygroscopic water. The samples tend to

230 equilibrate within ~2 days (Fig. 2). We suggest leaving the samples for a minimum of 54 hours,
231 which seems appropriate for re-equilibration. This is convenient for laboratory scheduling, as
232 soils may be removed from a drying oven, after drying overnight, and then be weighed with the
233 start of equilibration at ~9 am. Samples can be left to equilibrate for two days and then measured
234 around 3 pm or later to determine the water uptake.

235

236 **Effect of Organic Matter Removal on Water Adsorption at RH⁵⁰**

237 Hygroscopic water content as a function of the clay percentage of untreated and treated
238 Arizona soils that have had organic matter removed are presented in Fig. 3. The purpose of this
239 was to determine if the presence of organic matter strongly affected the relationship between the
240 hygroscopic water content and clay percentage. The removal of organic matter results in slightly
241 lower water adsorption, confirming that the clay percentage is the major factor in determining
242 the amount of water adsorbed. Based on the regression lines shown, and assuming that the
243 organic matter is largely responsible for any additional water adsorption, ~5 % difference in
244 organic matter for a soil with ~50 % clay may result in an 8 % difference in the estimated clay
245 percentage, which is acceptable for using field soil for a reconnaissance survey. This indicates
246 that for these soils, organic matter was not a major issue, but in future work we might want to
247 examine how different types of organic matter adsorb water and whether the relationship is
248 linear.

249 Fig. 4 compares the measurement error associated with determining the hygroscopic
250 water content of soil samples based on mass gained, with the measurement error associated with
251 determining clay content from sedimentation analysis using the hydrometer method. As
252 expected, the measurement errors are generally smaller at higher clay contents, with the % error

253 increasing rapidly at low clay contents. The error for the hygroscopic water content is generally
254 lower at low clay contents because our ability to weigh accurately is greater than our ability to
255 detect clay via sedimentation at low clay contents; from clay contents of 10-50 % the errors
256 involved are similar. This indicates that the greatest errors in estimating clay percentage from
257 hygroscopic water will be dependent on the spatial variability of organic matter, if not removed
258 from samples.

259

260 **Hygroscopic Water Content as a Function of Clay Content for Soils Equilibrated at RH⁵⁰**

261 Hygroscopic water content as a function of clay percentage for both the Arizona and
262 Trinidad soil data sets equilibrated at RH⁵⁰ is presented in Fig. 5. The Trinidad soils are divided
263 according to major mineralogy, kaolinitic, micaceous and mixed clays, sesquioxides and
264 montmorillonitic; the Arizona soils were dominated by mica and illite clay minerals. These soils
265 represent the range of 2:1 and 1:1 clay mineralogies (Table 1) and indicate strong consistency in
266 response compared to the trendlines indicated for the different pure clay minerals. The soils
267 dominated by sesquioxides and montmorillonite have distinctively higher hygroscopic water
268 content values than the other soils. The montmorillonite follows the bentonite trendline, whilst
269 the micaceous and mixed mineralogy follows the illite trendline. Noticeably the oxide dominated
270 soil follows the bentonite trendline indicating this soil can adsorb a lot of water; highly
271 weathered tropical soils with amorphous oxides can have large surface areas on which water can
272 adsorb (Sanchez, 1976; Goldberg et al., 2001; Robinson et al., 2009b). In addition, some of the
273 kaolinitic soils (clay content 50-70 %) have higher water content than might be expected. This
274 may occur due to the presence of oxides in these soils, biasing values upwards and requires
275 further research. The r^2 values for the regression equations of hygroscopic water content as a

276 function of clay content were 0.78 and 0.68 for Arizona soils and all Trinidad soils, respectively.
277 This indicates a positive linear relationship between hygroscopic water content and clay content
278 for soils of varying mineralogies, from temperate and tropical regions. The relationship was only
279 superior in the Arizona soils compared to the Trinidad soils due to less mineralogical variation.
280 The r^2 for the Trinidad soils increased to 0.84 after removing the oxide and montmorillonite
281 soils.

282 A compilation of available data sets that contain both clay percentage information and
283 hygroscopic water content (RH^{50}) for samples taken from landscapes mapped with the EMI
284 sensor in the USA and Trinidad, are presented in Fig. 6. The results fall broadly in the same
285 location as in Fig. 5. The r^2 values with intercept set to zero, RMSE and corresponding
286 mineralogy are presented in Table 2. The r^2 values improve as the range of the clay percentage
287 broadens. All RMSE values for clay percentage as a function of RH^{50} fall below 10 % with the
288 median value being 5 %. This indicates that for these soils, RH^{50} was a reasonable predictor of
289 clay percentage. Placing a regression line through all data ($\text{clay \%} = 1037.5 * RH^{50}$) gave an r^2 of
290 0.70 and resulted in a RMSE of 6.5 % which may be acceptable for reconnaissance survey.
291 However, we do not advocate the use of a single relationship as it is mineralogy dependent. In
292 this regard a site specific calibration should be established between RH^{50} and clay percentage
293 that could then be used to estimate clay percentage from subsequent samples measured only for
294 RH^{50} . RH^{50} values would be useful for providing secondary data, in for example co-kriging
295 geostatistical methods (Lesch et al., 1995a). The results indicate reasonable correlations,
296 demonstrating that hygroscopic water content at RH^{50} has good potential to act as a pedotransfer
297 function to estimate clay percentage at least for reconnaissance surveys and as a secondary
298 variable for geostatistical interpolation.

299 **DISCUSSION**

300 Developing a standard approach to estimating clay percentage from the hygroscopic
301 water content relies on agreeing on an accepted relative humidity value at which to measure the
302 hygroscopic water content. Different authors have used different values, Banin and Amiel (1970)
303 used air dry samples, whilst Petersen et al. (1996) used a pressure of 1.5 MPa. Logsdon et al.
304 (2010) determined hygroscopic water content of air dry soils in a vapor-tight container over
305 distilled water at ~99 % relative humidity. In an effort to standardize a method, Lebron et al.
306 (2009), used a hygroscopic water content of 41 % to determine gypsum content in soils. They
307 used 41 % because this is the relative humidity achieved by equilibrating samples over a
308 saturated solution of K_2CO_3 in a dessicator, which makes standardization easier, especially given
309 the temperature stability of the RH of K_2CO_3 . However, finding a salt that offers a temperature
310 stable RH at ~50-60% is not straightforward. Any chosen value of RH is a trade-off between
311 having a zone of minimal relative change of slope of the water release curve of the soil (Fig. 1),
312 and having enough water to obtain a meaningful measurement of hygroscopic water content.
313 RH^{50} was chosen as a compromise, bearing in mind this trade-off, which seems to work
314 reasonably well even in kaolinitic soils. The use of K_2CO_3 is appealing and good for 2:1 clay
315 mineral soils, but is not so good for kaolinitic soils which have essentially desorbed all their
316 water at RH 41%.

317 The benefits of proximal sensing techniques in reconnaissance surveys have, to some
318 extent, been undermined by the cost and tedious requirements for soil sampling and analysis of
319 properties such as clay percentage required for their calibration. The removal of organic matter
320 from the samples in the current study resulted in only minimal reduction in adsorbed water (Fig.
321 4). This signifies that in soils low organic matter, clay percentage is the major factor in

322 determining the amount of water adsorbed. Clay percentage has been shown by previous workers
323 to be strongly correlated with specific surface area and hygroscopic water content (e.g., Banin
324 and Amiel, 1970; Petersen et al., 1996; Robinson et al., 2002). However, hygroscopic water
325 content which is a quicker and cheaper soil property to measure is often not routinely collected
326 by soil surveys (Robinson et al., 2002). Since the amount of water adsorbed by a sample varies
327 depending on the ambient humidity, finding a suitable relative humidity for the equilibration of
328 soils is important for the determination of hygroscopic water content to speed up the
329 interpretation of geophysical signals. In our study, RH^{50} was chosen as a compromise value from
330 the determination of hygroscopic water content for standard clays which generally yielded
331 hygroscopic water content values that were strongly correlated with clay percentage for both
332 tropical and temperate soils of varying mineralogies.

333

334

335 **SUMMARY AND CONCLUSIONS**

336

337 The work presented describes a simple, cost and time efficient method of estimating clay
338 content using hygroscopic water content measurements. To successfully determine the
339 relationship between hygroscopic water content and clay content it is important to identify a
340 suitable value of relative humidity for equilibration of soils. Based on our results on water
341 release curves of standard clay minerals, this value was identified to be ~50 %, a relatively stable
342 point at which the change in hygroscopic water content with humidity is at a minimum. This
343 value was then used to equilibrate soil samples from tropical (Trinidad) and temperate (Arizona)
344 regions exhibiting a wide range of soil mineralogy.

345 The work presented indicates positive correlations between soil hygroscopic water
346 content measured at RH⁵⁰ and the clay percentage in the soil. Hygroscopic water content
347 measured at RH⁵⁰ has good potential to act as a pedotransfer function to estimate clay percentage
348 for surveys. One of three approaches, with increasing accuracy, could be adopted:

349 1) estimate clay percentage from the linear hygroscopic water content calibration
350 presented for all soils.

351 2) perform a site specific calibration on a soil subsample between clay and relative
352 humidity.

353 3) perform a full calibration using particle size analysis.

354

355 With the growth of proximal sensing the first approach offers a cheap and rapid way to
356 estimate the dependence of soil geophysical signal response surfaces to hygroscopic water
357 content as a surrogate for soil clay percentage for reconnaissance survey. This may guide a
358 surveyor as to the major soil parameter contributing to the geophysical signal response.

359

REFERENCES

360 Abdu, H., D.A. Robinson, M. Seyfried, and S.B. Jones. 2008. Geophysical imaging of watershed
361 subsurface patterns and prediction of soil texture and water holding capacity. *Water*
362 *Resour. Res.* 44, W00D18, doi:10.1029/2008WR007043.

363 Banin, A., and A. Amiel. 1970. A correlative study of the chemical and physical properties of a
364 group of natural soils of Israel. *Geoderma* 3:185-198.

365 Briggs, L.J., and H. L. Shantz. 1912. The wilting coefficient and its indirect determination. *Bot.*
366 *Gaz.* 53:20-37.

367 Crave, A., and C. Gascuel-Oudou. 1997. The influence of topography on time and space

368 distribution of soil surface water content. *Hydrol. Proc.* 11:203–210.

369 Dirksen, C., and S. Dasberg, 1993. Improved calibration of time domain reflectometry soil water
370 content measurements. *Soil Sci. Soc. Am. J.* 57: 660-667.

371 Doolittle, J.A., K.A. Sudduth, N.R. Kitchen, and S.J. Indorante. 1994. Estimating
372 depths to claypans using electromagnetic induction methods. *J. Soil Water Conserv.*
373 49:572–575.

374 Friedman, S.P. 2005. Soil properties influencing apparent electrical conductivity: A review.
375 *Comput. Electron. Agric.* 46:45–70.

376 Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383–411. In A. Klute (ed.) *Methods*
377 *of soil analysis. Part 1.* 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

378 Goldberg, S., and R.A. Glaubig. 1987. Effect of saturating cation, pH, and aluminum and iron
379 oxide on the flocculation of kaolinite and montmorillonite. *Clays and Clay Min.* 35:220-
380 227.

381 Goldberg, S., I. Lebron, D.L.Suarez, and Z.R. Hinedi. 2001. Surface characterization of
382 amorphous aluminium oxides. *Soil Sci. Soc. Am. J.* 65:78-86.

383 Grayson, R., and G. Bloschl. 2000. *Spatial Patterns in Catchment Hydrology: Observations and*
384 *Modeling.* Cambridge University Press: Cambridge.

385 Harvey, O.R., and C. L. S. Morgan. 2008. Predicting regional-scale soil variability using a single
386 calibrated apparent soil electrical conductivity model. *Soil Sci. Soc. Am. J.* 73:164-169.

387 Lebron, I., J. Herrero, and D.A. Robinson. 2009. Determination of gypsum content in
388 soils exploiting the gypsum-bassanite phase change. *Soil Sci. Soc. Am. J.* 73:403–411.

389 Lesch, S.M., D.J. Strauss, and J.D. Rhoades. 1995a. Spatial prediction of soil salinity using
390 electromagnetic induction techniques: 1. Statistical prediction models—A comparison of
391 multiple linear regression and cokriging. *Water Resour. Res.* 31:373–386.

392 Lesch, S.M., D.J. Strauss, and J.D. Rhoades. 1995b. Spatial prediction of soil salinity using
393 electromagnetic induction techniques: 2. An efficient spatial sampling algorithm suitable
394 for multiple linear regression model identification and estimation. *Water Resour. Res.*
395 31:387–398.

396 Lesch, S.M., J.D. Rhoades, and D.L. Corwin. 2000. ESAP-95 Version 2.01R: User
397 17 manual and tutorial guide. Res. Rep. 146. USDA-ARS George E. Brown, Jr., Salinity
398 Lab., 18 Riverside, CA.

399 Logsdon, S., T.R. Green, M. Seyfried, S.R. Evett, and J. Bonta. 2010. Hydra probe and twelve-
400 wire probe comparisons in fluids and soil cores. *Soil Sci. Soc. Am. J.* 74:5-12.

401 Petersen, L.W., P. Moldrup, O.H. Jacobsen, and D. Rolston. 1996. Relations between specific
402 surface area and soil physical and chemical properties. *Soil Sci.* 161:9-21.

403 Quirk, J.P., and R. S. Murray. 1999. Appraisal of the ethylene glycol monoethyl ether method for
404 measuring hydratable surface area of clays and soils. *Soil Sci. Soc. Am. J.* 63:839-849.

405 Rawlins, B.G., R. M. Lark, and R. Webster. 2007. Understanding airborne radiometric survey
406 signals across part of eastern England. *Earth Surf. Proc. Landforms.* 32:1503–1515.

407 Resurreccion, A.C., P. Moldrup, M. Tuller, T.P.A. Ferre, K. Kawamoto, T. Komatsu, and L.W.
408 de Jonge. 2011. Relationship between specific surface area and the dry end of the water
409 retention curve for soils with varying clay and organic carbon contents. *Water Resour.*
410 *Res.*, 47, W06522, doi:10.1029/2010WR010229.

411 Robinson, D.A., J.D. Cooper, and C.M.K. Gardner. 2002. Modelling the relative permittivity of
412 soils using soil hygroscopic water content. *J. Hydrol.* 255:39-49.

413 Robinson, D.A., C.S. Campbell, J.W. Hopmans, B.K. Hornbuckle, S.B. Jones, R. Knight, F.
414 Ogden, J. Selker, and O. Wendroth. 2008a. Soil moisture measurement for ecological and
415 hydrological watershed scale observatories: A review. *Vadose Zone J.* 7:358–389.

416 Robinson, D.A. A. Binley, N. Crook, F.D. Day-Lewis, T.P.A. Ferre, V.J.S. Grauch R. Knight,
417 M. Knoll, V. Lakshmi, R. Miller, J. Nyquist, L. Pellerin, K. Singha, and L. Slater. 2008b.
418 Advancing process-based watershed hydrological research using near-surface
419 geophysics: A vision for, and review of, electrical and magnetic geophysical methods.
420 *Hydrol. Proc.* 22:3604-3635.

421 Robinson, D.A., L. Lebron, and H. Vereecken. 2009a. On the definition of the natural capital of
422 soils: A framework for description, evaluation and monitoring. *Soil Sci. Soc. Am. J.*
423 73:1904-1911.

424 Robinson, D.A., S.B. Jones, J.M. Jr. Blonquist, R. Heinse, I. Lebron, and T.E. Doyle. 2009b. The
425 dielectric response of the tropical Hawaiian Mars soil simulant JSC Mars-1. *Soil Sci. Soc.*
426 *Am J.* 73:1113–1118.

427 Samouelian, A., I. Cousin, A. Tabbagh, A. Bruand, and G. Richard. 2005. Electrical resistivity
428 survey in soil science: A review. *Soil Tillage Res.* 83:173–
429 193.

430 Sanchez, P.A. 1976. *Properties and management of soils in the tropics*. John Wiley, New York.

431 Schaap, M.G., F.J. Leij, and M. Th. van Genuchten. 2001. Rosetta: a Computer Program for
432 Estimating Soil Hydraulic Parameters with Hierarchical Pedotransfer Functions. *J.*
433 *Hydrol.* 251:163-176.

434 Slater L., D. Ntarlagiannis, and D. Wishart. 2006. On the relationship between induced
435 polarization and surface area in metal-sand and clay-sand mixtures. *Geophysics* 71: A1–
436 A5.

437 Schjonning, P., I.K. Thomsen, P. Moldrup, and B.T. Christensen. 2003. Linking soil microbial
438 activity to water- and air-phase contents and diffusivities. *Soil Sci. Soc. Am. J.* 67:156–
439 165.

440 Sudduth, K.A., N.R. Kitchen, W.J. Wiebold, W.D. Batchelor, G.A. Bollero, D.G. Bullock, D.E.
441 Clay, H.L. Palm, F.J. Pierce, R.T. Schuler, and K.D. Thelen. 2005. Relating apparent
442 electrical conductivity to soil properties across the north-central USA. *Comput. Electron.*
443 *Agric.* 46:263–283.

444 Taylor, M.J., K. Smettem, G. Pracilio, and W. Verboom. 2002. Relationships between soil
445 properties and high-resolution radiometrics, central eastern Wheatbelt, Western Australia.
446 *Exploration Geoph.* 33: 95-102

447 Triantafilis J., I.A. Huckel, and I.O.A. Odeh. 2001. Comparison of statistical prediction methods
448 for estimating field-scale clay content using different combinations of ancillary variables.
449 *Soil Sci.* 166:415–427.

450 Triantafilis, J., and S.M. Lesch. 2005. Mapping clay content variation using electromagnetic
451 induction techniques. *Comput. Electron. Agric.* 46:203–237.

452 Tuller M., and D. Or. 2005. Water films and scaling of soil characteristic curves at low water
453 contents. *Water Resources Research* 41. DOI: W0940310.1029/2005wr004142.

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456 **Table 1. USDA textural class, clay percentage and mineralogy of 23 tropical soils from the**
 457 **soil collection of the University of the West Indies, Trinidad and 20 temperate soils from**
 458 **the soil collection of the University of Arizona, USA.**
 459

University of the West Indies soil collection			University of Arizona soil collection		
USDA textural class	Clay content (%)	Clay minerals	USDA textural class	Clay content (%)	Clay minerals
Sandy Loam	15	Kaolinitic	Coarse Sand	1	-
Sandy Loam	17	Micaceous	Fine Sand	2	-
Sandy Loam	18	Kaolinitic	Loamy Coarse Sand	6	Micaceous
Sandy Loam	19	Micaceous	Loamy Sand	10	Micaceous
Sandy clay Loam	27	Micaceous	Loamy Fine Sand	5	Micaceous
Sandy clay Loam	27	Mixed	Fine Sandy Loam	7	Illitic
Sandy clay Loam	29	Kaolinitic	Sandy Loam	15	Micaceous
Sandy clay Loam	29	Kaolinitic	Fine Sandy Loam	12	Micaceous
Sandy clay Loam	29	Kaolinitic	Loam	19	Illitic
Sandy clay Loam	29	Kaolinitic	Silt Loam	20	Micaceous
Sandy clay Loam	33	Kaolinitic	Silt Loam	20	Micaceous
Sandy clay Loam	35	Mixed	Loam	24	Micaceous
Clay Loam	35	Mixed	Sandy Clay Loam	25	Micaceous
Sandy clay	43	Oxidic	Sandy Clay Loam	31	Micaceous
Clay	45	Mixed	Clay Loam	36	Micaceous
Clay	51	Mixed	Silty Clay Loam	35	Micaceous
Clay	55	Kaolinitic	Silty Clay Loam	34	Micaceous
Clay	57	Mixed	Silty Clay	52	Illitic
Clay	63	Kaolinitic	Clay	54	Illitic
Clay	66	Kaolinitic	Sandy Clay	39	Micaceous
Clay	67	Mixed			
Clay	71	Montmorillonitic			
Clay	82	Mixed			

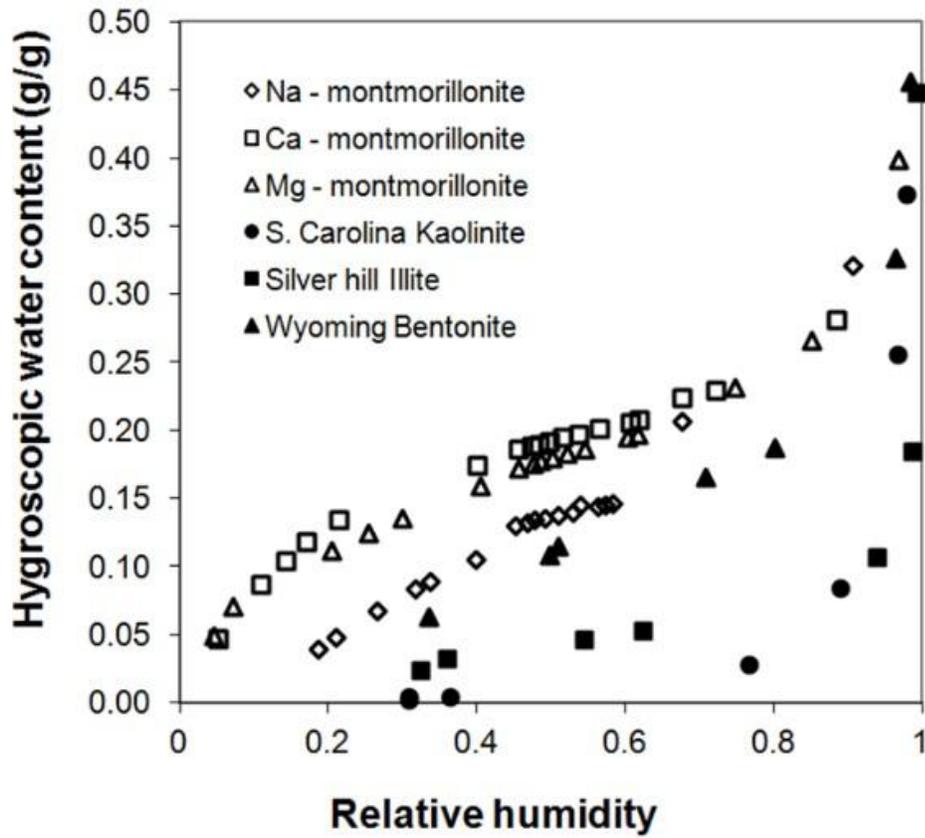
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461 **Table 2. RMSE for the prediction of clay percentage from the RH^{50} values for a selection of**
 462 **soils and the dominant mineralogy.**

Soil sampling location	r^2 (No. of samples)	Clay % RMSE	Dominant mineralogy
Moruga, Trinidad	0.40 (40)	6.6	Mixed
Guayaguayare, Trinidad	0.62 (46)	4.0	Kaolinitic
Woodland, Trinidad	0.40 (67)	9.0	Montmorillonitic
Centeno, Trinidad	0.87 (123)	6.2	Mixed
TW Daniels, Utah	0.63 (15)	3.5	Montmorillonitic
Reynolds Creek, Idaho	0.48 (17)	4.2	Montmorillonitic

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464



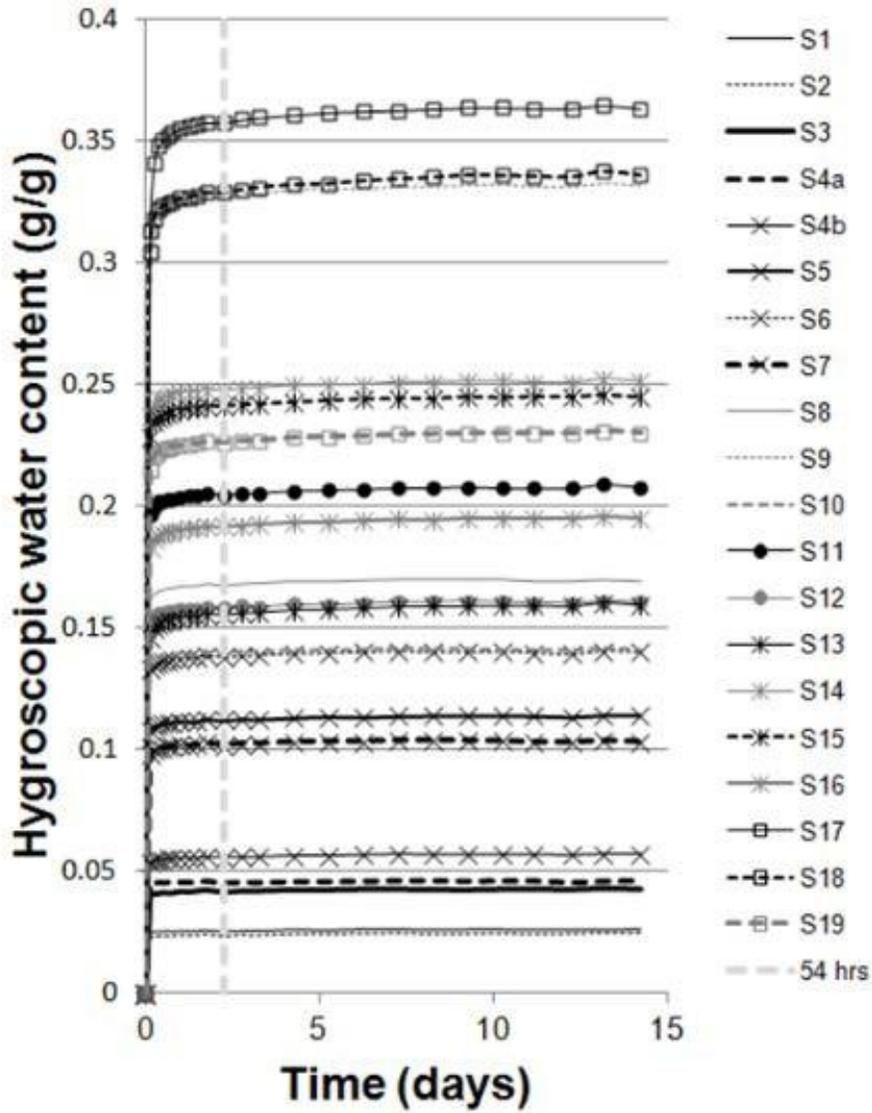
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466 Fig. 1. Water release curves for standard clays.

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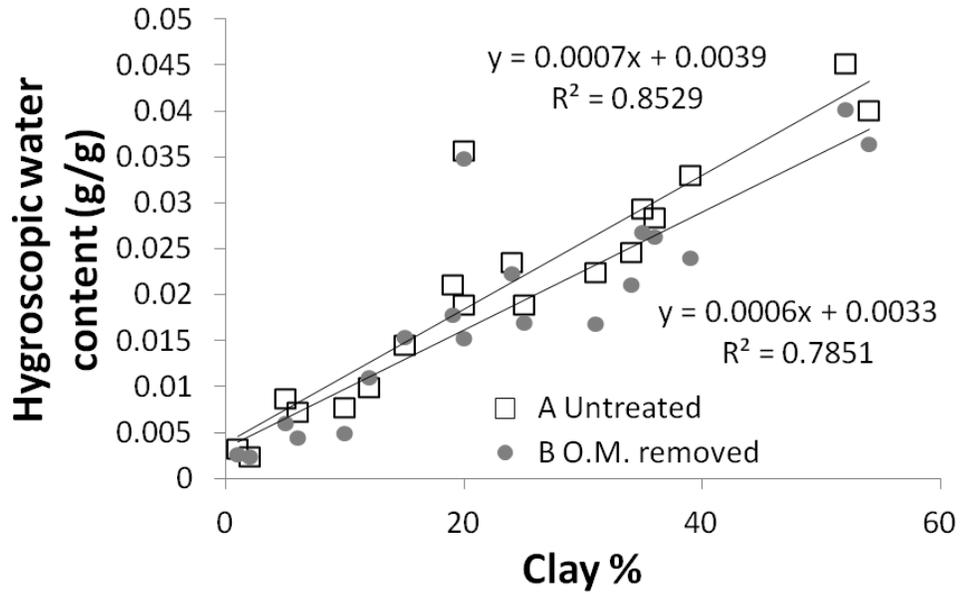


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471 Fig. 2. Water uptake on treated temperate Arizona soils at 25°C indicating water is rapidly
 472 adsorbed in 48hrs.

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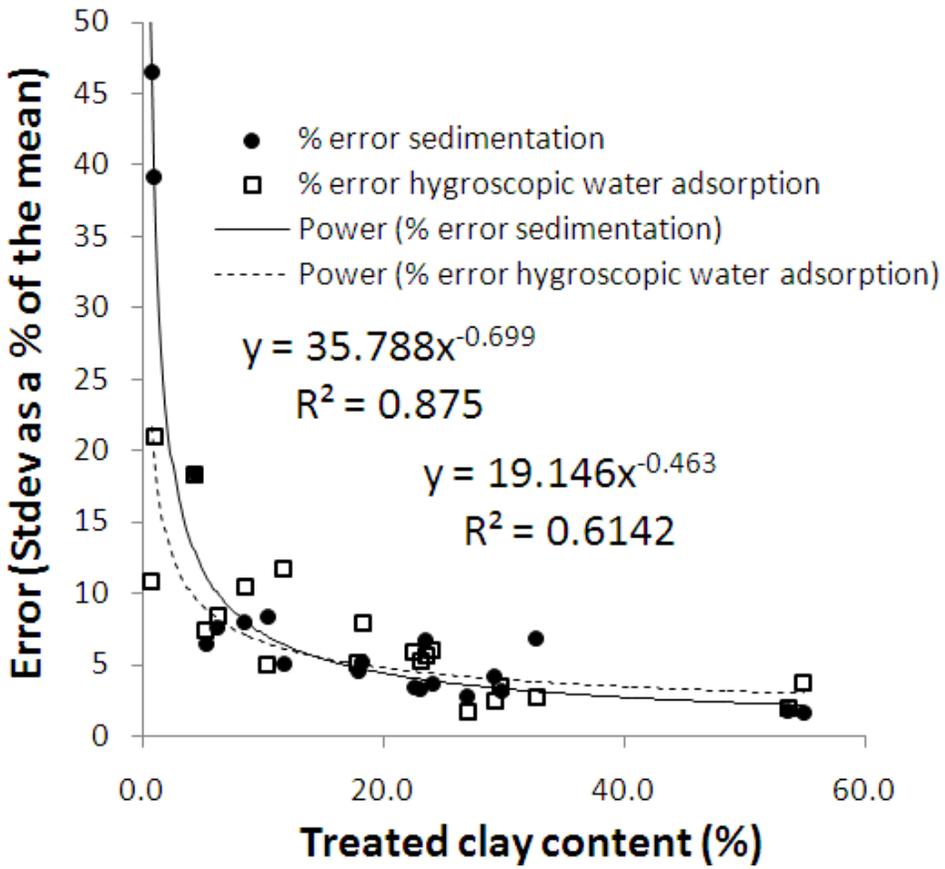
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477 Fig. 3. Hygroscopic water content as a function of the clay percentage comparing untreated and

478 treated temperate Arizona soils that have had organic matter (O.M.) removed.

479

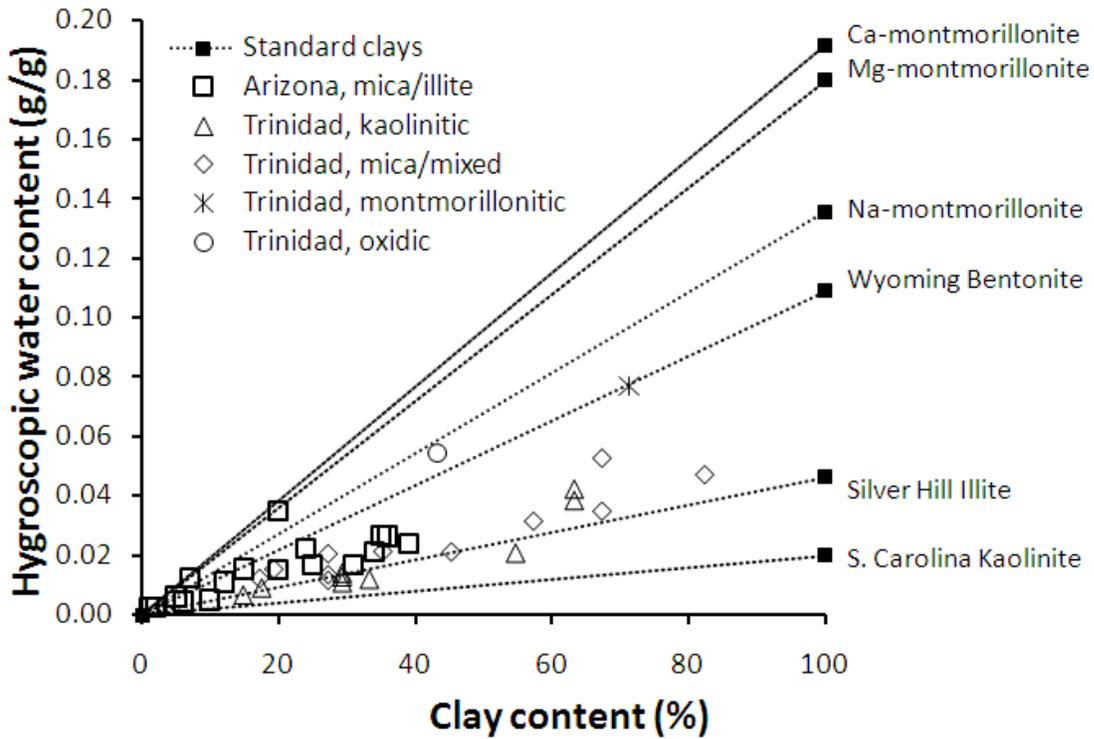
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482 Fig. 4. Trinidad and Arizona soils error as a function of the treated (organic matter removed) clay
483 percentage; the error is represented as the standard deviation (stdev) as a percentage of the mean
484 of 4 independent replicates.

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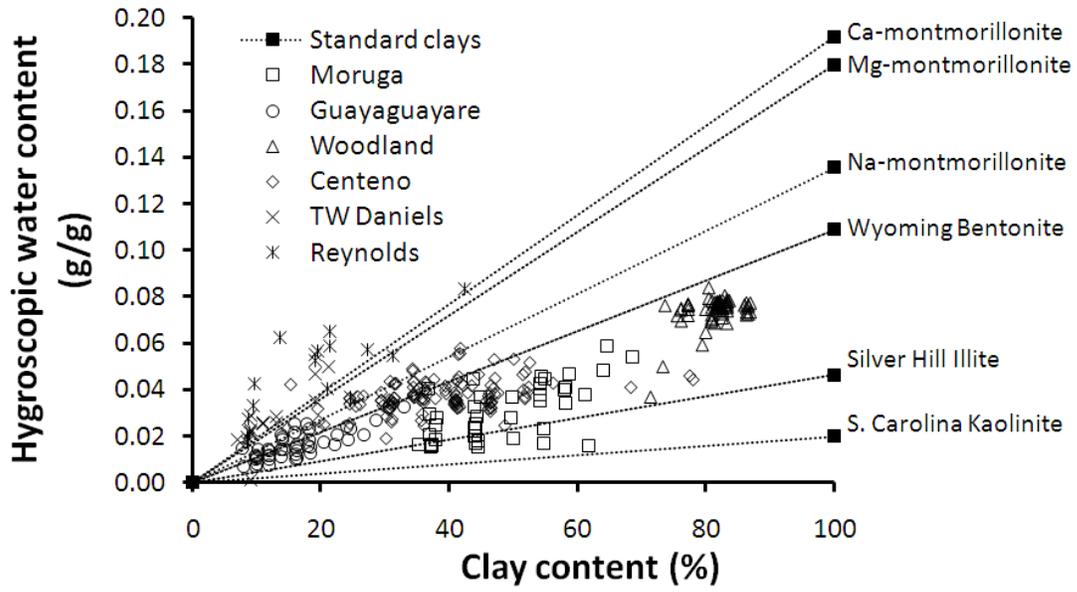
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489 Fig. 5. Hygroscopic water content (RH^{50}) as a function of clay percentage for 23 tropical
 490 Trinidad soils divided by major mineralogy, 20 temperate Arizona soils, and 100 % clay
 491 samples. The dashed linear trend lines join the 100% clay samples to the origin as a guide for
 492 comparison with figure 6.

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498 Fig. 6. Five data sets showing field scale variability; one data set from a soil dominated by Ca
 499 montmorillonite from Utah and four from Trinidad. The dashed linear trend lines join the 100%
 500 clay samples to the origin as a guide for comparison with figure 5. For r^2 and RMSE see Table 2.