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MDPI

Article: Supplementary Information

Empower innovations in routine soil testing

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In this supplementary information file, we present additional data and information related to:

Figure S1. Scatter plots of the results of NIRS determinations versus the results derived from conventional analyses procedures (right-hand figures) and scatter plots of the residual variance of these relationships (left-hand figures), for N-total, S-total, Ca-CEC, SOM, SOC, C-inorganic, Clay, CEC, pH, Sand, K-CEC, Mg-CEC: validation data set.

Table S1. Statistics of the calibration of NIRS to the results of the conventional methods. A distinction has been made between soil characteristics that have been implemented into laboratory practice for routine soil testing, and soil characteristics that are still in the phase of further testing (and thus have not yet been implemented into laboratory practice for routine soil testing); calibration data set.

S1. NIRS Reference methods

NIRS analyses were calibrated to results of reference (conventional) analytical methods. N-total, and S-total were determined following Dumas's combustion with an elemental analyzer (dry combustion method) [125]. Effective CEC, K-CEC, Mg-CEC, Ca-CEC, Na-CEC, and Mn-CEC were determined by means of cobalt hexamine trichloride extractions followed by ICP-AES and AAS [126,127], and pH-$CaCl_2$ according ISO 10390 (2005) [128]. Soil organic matter (SOM) is determined by loss on ignition (550 °C) [129], soil organic carbon (SOC) as elemental C following dry combustion (550°C) [130-132], and total carbon (TC) which includes SOC and soil inorganic carbon (SIC) by dry combustion at 1150 °C [133]. Soil inorganic carbon (SIC) is determined by acidification [133]. Moisture content (to 40 °C) and dry matter content (from 40 – 103°C) of soil was done according NEN 5748, 1990 [134]. For NIRS calibration and validation measurement quality improvement (not as a reference) the loss of ignition procedure is also performed directly in the 40°C dried sample, so without oven drying from 40°C – 103°C. Plant available calcium and electric conductivity were determined with 1:2 water [135]. Clay content was determined through density fractionation [136,137]. Clay (< 2 um) was also measured as part of the particle size analyses together with silt (2-16, and 16-50 um) and several sand fractions (50 – 2000 μm) (pipet and sieve after removal of salts and organic matter by hydrogen peroxide) [137]. The median grain size of the sand fraction (M50) was calculated based on these sand fractions. Dissolved organic nitrogen (DON) was measured in 0.01 M $CaCl_2$ ([138]. Oxalate extractable Al, Fe, and P were determined[139,140] and used for P-binding and P-saturation (so both calculation based on oxalate extractable Al, Fe, and P). P-total was measured [141,142].

S2. NIRS Calibration procedures

For relating the NIR-signals to reference results, calibration models were developed. The first soil models at Eurofins Wageningen were built in 2003, and in 2004 the first soil characteristics (N-total, and SOM) [86] were routinely offered to the soil testing market. The calibration has been continuously improved since then. Soil samples with a too large Mahalanobis distance (distance of an unknown sample to the middle of the local selected calibration samples) are considered outliers and subsequently analyzed by the reference methods (and these results are reported, and also added to the calibration data base). In addition, 18 soil samples are - ad randomly - selected weekly and analyzed by the reference methods (at least in duplicate). Part of these results are used to improve the calibration, and part is used for validation.

S3. NIRS Validation procedures

A separate set of data has been created for validation of the NIRS models. The data are not used for calibrations. The validation database we describe here contains roughly between 1500 and 2000 reference samples, depending on the year of introduction of the soil characteristics.

S4. Quality control of soil testing

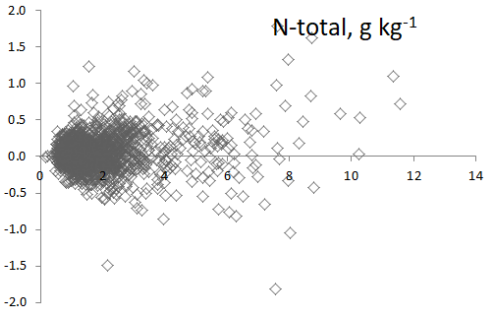
To establish the quality and reproducibility of the different soil characteristics, the results of analytical procedures are subject to quality assessment and assurance. This quality control is subdivided in first-, second- and third-line control procedures. The first-line control is performance checking by the laboratory analysts, using standard soil samples with well-known results. When the results of the standard soil samples exceed twice the standard deviation (95.5% of the results are within ± 2 s.d.) a notice will be made. When the results exceed three times the standard deviation (99.7% of the results are within ± 3 s.d.) the following step are taken i) investigation into the cause of the variation, ii) results are not reported iii) all samples of this batch are re-analyzed after the problem has been solved and the results meet the requirements, and iv) all results are recorded in a logbook. The second-line control is a check within the laboratory but independent of the executors (so the results of these control samples are not known to the analysist). The third-line control is an independent external check, a ring test. Eurofins Agro participates in the ring tests of ILVO (www.ilvo.vlaanderen.be), VITO (www.vito.be), and Wepal (http://www.wepal.nl/website/products/ISE.htm). Both second and third line controls are part of NEN-EN-ISO 17025, 2018 [143] for which the laboratory is accredited.

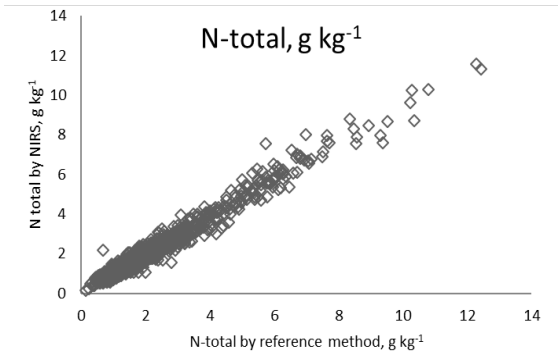
S5. Scientific underpinning of the $CaCl_2$ method

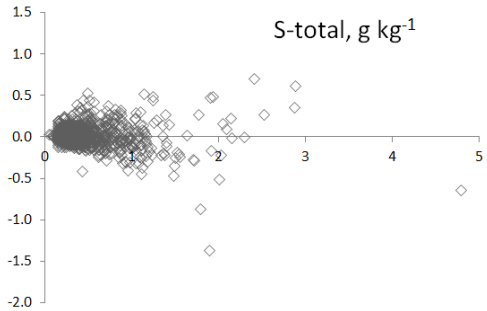
The multi-nutrient extractant 0.01 M $CaCl_2$ method is used worldwide and embedded in many scientific testing programs and papers [144]. To illustrate the case further, the 0.01 M $CaCl_2$ extraction method has been used for testing Si fertilization of sugar cane in South Africa [145], for testing K fertilization of rice in Iran [146] and finger millet in India [147], for testing Mn fertilization in tea in Turkey [148], and for testing S fertilization of various field and forage crops

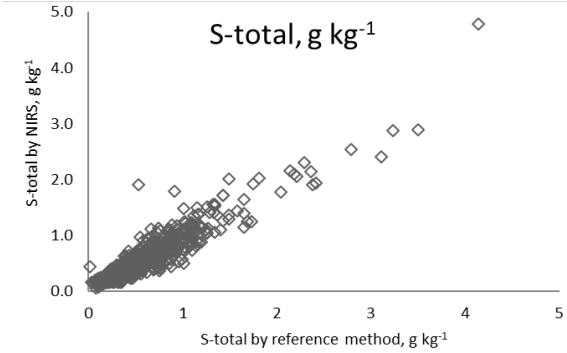
in USA [149]. These reports indicate that the 0.01 M $CaCl_2$ extraction method is diagnostic for identifying fertilization needs of a wide range of soil, crop and nutrient element combinations.

The multi-nutrient extractant 0.01 M $CaCl_2$ method [150,151] was also tested in The Netherlands in several field trials for maize (Zea mays) grassland (Lolium perenne), and arable crops and vegetable crops [152-154]. Further, a large number of archived soil samples from Germany (arable crops) was re-analysed at the Eurofins laboratory in Wageningen and related to results from field experiments in Germany [155]. Also, results from 250 fertilization experiments were related to the results of thousands of re-analysed soil samples from the archive of Wageningen University TAGA [156], and the resulting relationships were used for new crop, and soil based fertilization recommendation. Meanwhile further desk studies and field trials were performed and are still in process for K, and Mg [157-162]. Also validation studies were performed; soil N-tests (e.g. dissolved organic nitrogen extracted with $CaCl_2$) and their role in N-fertilization recommendations were extensively investigated [163-165]. Relations between selenium (Se-$CaCl_2$), plant uptake and fertilization of both grassland and arable land were studied by Supriatin [166,167].


N-total, g kg-1


N-total, g kg-1
N total by NIRS, g kg-1
N-total by reference method, g kg-1


S-total, g kg-1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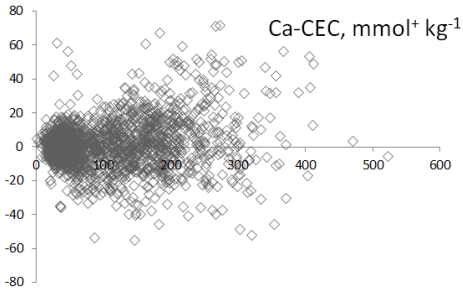
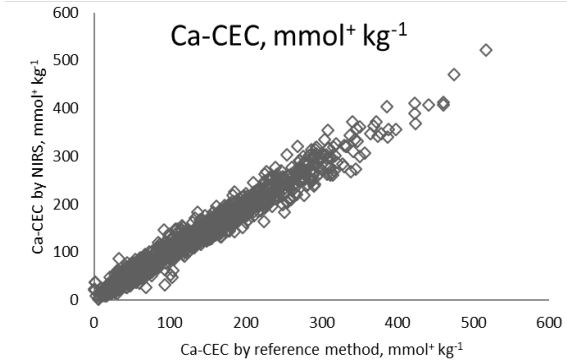
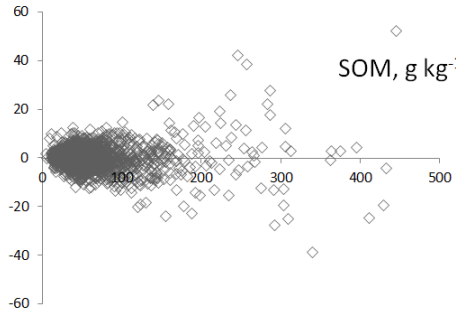
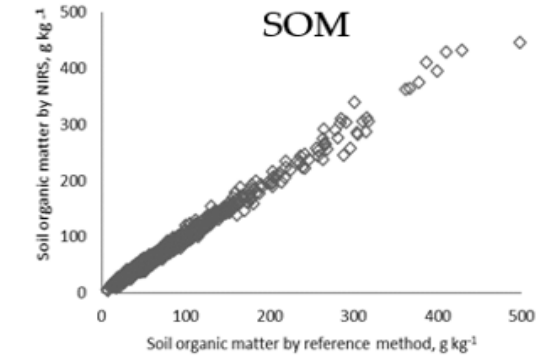
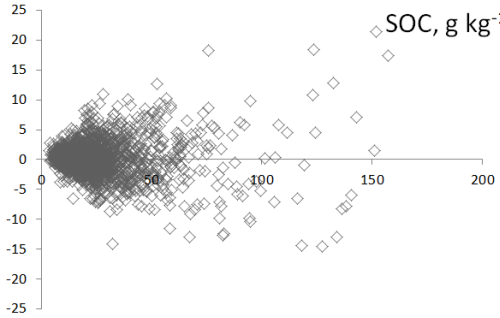
S-total by NIRS, g kg-1
S-total by reference method, g kg-1

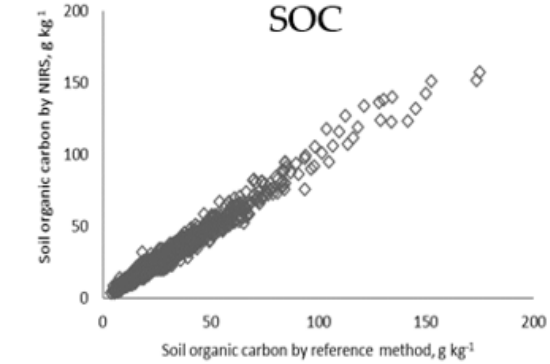

Ca-CEC, mmol+ kg-1

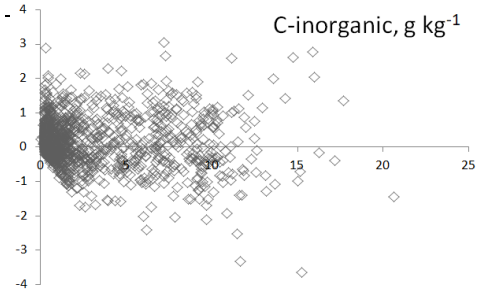

Ca-CEC, mmol+ kg-1
Ca-CEC by NIRS, mmol+ kg-1
Ca-CEC by reference method, mmol+ kg-1

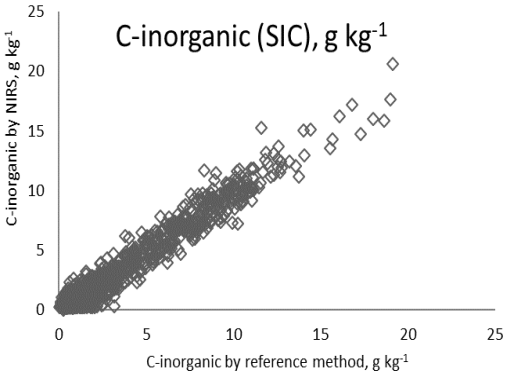

SOM, g kg-1

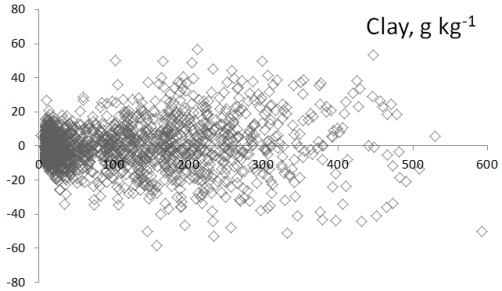

SOM
Soil organic matter by NIRS, g kg-1
Soil organic matter by reference method, g kg-1

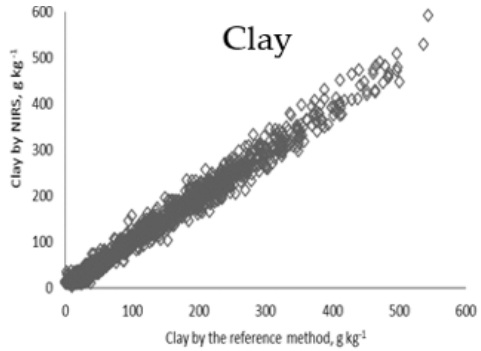

SOC, g kg-1

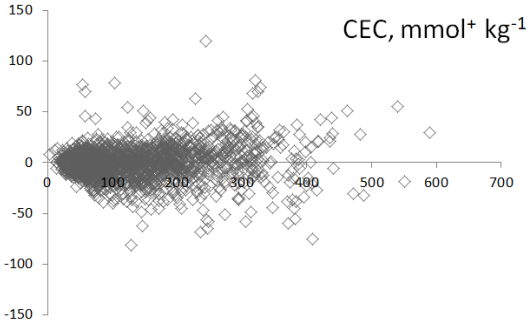

SOC
Soil organic carbon by NIRS, g kg-1
Soil organic carbon by reference method, g kg-1

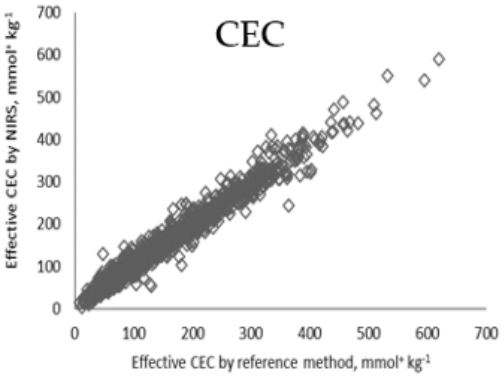

C-inorganic, g kg-1

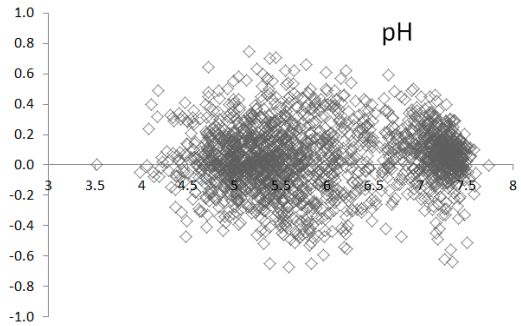

C-inorganic (SIC), g kg-1
C-inorganic by NIRS, g kg-1
C-inorganic by reference method, g kg-1

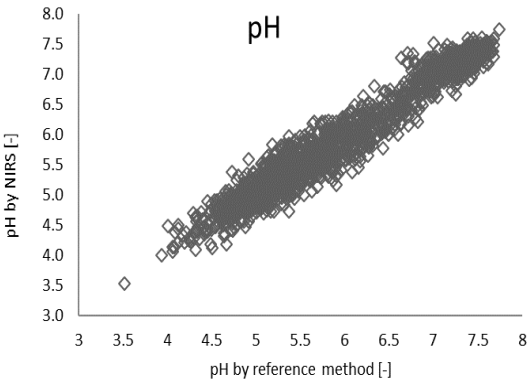

Clay, g kg-1

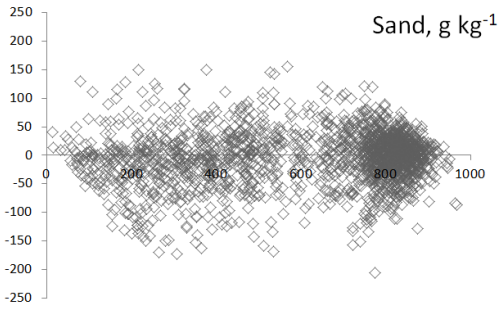

Clay
Clay by NIRS, g kg-1
Clay by the reference method, g kg-1

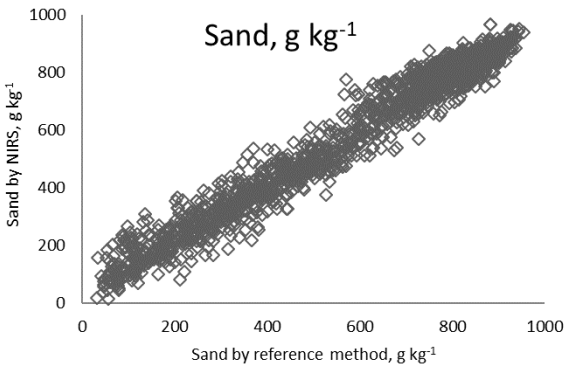

CEC, mmol+ kg-1

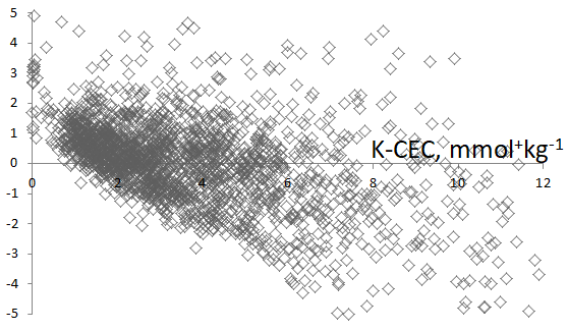

CEC
Effective CEC by NIRS, mmol+ kg-1
Effective CEC by reference method, mmol+ kg-1

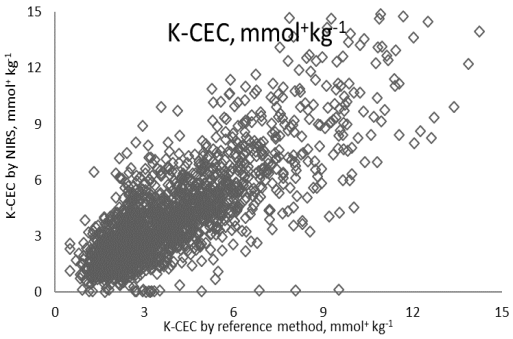

pH

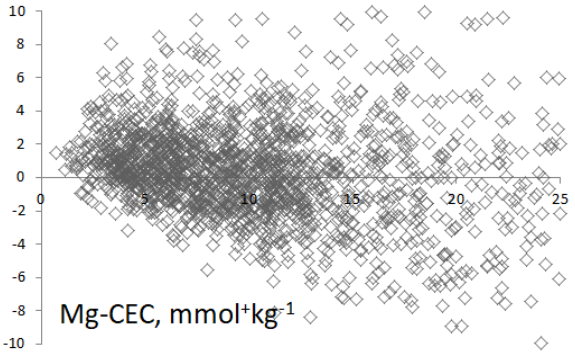

pH
pH by NIRS [-]
pH by reference method [-]


Sand, g kg-1
250
200
150
100
50
0
-50
-100
-150
-200
-250
0
200
400
600
800
1000


Sand, g kg-1
Sand by NIRS, g kg-1
1000
800
600
400
200
0
0
200
400
600
800
1000
Sand by reference method, g kg-1


K-CEC, mmol+kg-1
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8
10
12


K-CEC, mmol+kg-1
K-CEC by NIRS, mmol+ kg-1
15
12
9
6
3
0
0
3
6
9
12
15
K-CEC by reference method, mmol+ kg-1


Mg-CEC, mmol+kg-1
10
8
6
4
2
0
-2
-4
-6
-8
-10
0
5
10
15
20
25

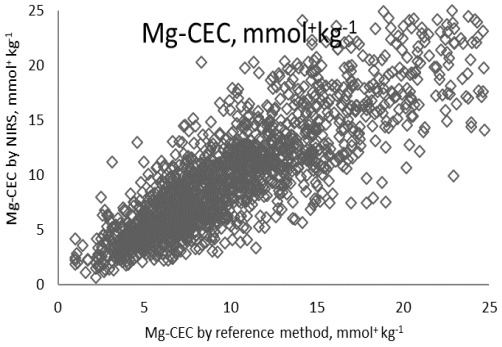

Mg-CEC, mmol+kg-1
Mg-CEC by NIRS, mmol+ kg-1
25
20
15
10
5
0
0
5
10
15
20
25
Mg-CEC by reference method, mmol+ kg-1

Figure S1. Scatter plots of the results of NIRS determinations versus the results derived from conventional analyses procedures (right-hand figures) and scatter plots of the residual variance of these relationships (left-hand figures), for N-total, S-total, Ca-CEC, SOM, SOC, C-inorganic, Clay, CEC, pH, Sand, K-CEC, Mg-CEC: validation data set.

Table S1. Statistics of the calibration of NIRS to the results of the conventional methods. A distinction has been made between soil characteristics that have been implemented into laboratory practice for routine soil testing, and soil characteristics that are still in the phase of further testing (and thus have not yet been implemented into laboratory practice for routine soil testing). PMN = potentially mineralizable nitrogen [168]: calibration data set.

Soil characteristic	calibration						
Implemented	n	r^2	year	Bias	RPD	Sres	RMSD
N-total	55947	0.99	2004	0.002	8.6	0.53	0.53
S-total	37783	0.97	2004	-0.000	5.5	0.21	0.21
K-CEC	16144	0.79	2006	-0.040	2.0	2.19	2.19
Ca-CEC	15742	0.97	2006	0.483	5.5	17.52	17.53
Mg-CEC	15732	0.88	2006	-0.015	2.7	6.32	6.32
pH-$CaCl_2$	89075	0.97	2013	-0.004	5.3	0.18	0.18
SOC	21976	0.99	2004	0.066	12.9	4.93	4.93
SOM	24825	1.00	2004	0.007	17.5	6.46	6.46
SIC	15864	0.97	2004	0.001	5.6	1.45	1.45
Clay	49121	0.98	2004	0.664	7.0	17.97	17.99
Sand	8419	0.96	2015	1.390	4.7	58.37	58.39
ECEC	16122	0.97	2005	0.125	5.8	20.44	20.44
In process/ not reported							
DON-$CaCl_2$	4421	0.89	-	0.788	2.8	28.26	28.27
PMN	7897	0.88	2007	0.816	2.7	21.58	21.60
P-total	4280	0.95	-	-0.119	4.2	26.63	26.63
P-oxalate	7477	0.74	-	-0.067	1.7	5.80	5.81
Al-oxalate	7478	0.95	-	-0.109	4.1	12.66	12.66
Fe-oxalate	7498	0.91	-	0.126	3.1	24.12	24.12
P-binding	4853	0.93	-	0.020	3.5	13.70	13.70
P-saturation	4853	0.68	-	0.222	1.6	12.71	12.72
P-Al (Brolsma et al., 2018)	113,072	0.83	2014	0.770	2.6		
Ca-water	2567	0.87	2015	0.019	2.6	0.93	0.93
Na-CEC	10238	0.77	2006	-0.008	1.8	0.71	0.71
Mn-CEC	7243	0.69	-	0.011	1.5	0.32	0.32
EC	3433	0.77	-	0.011	1.8	0.37	0.37
TC	5870	1.00	-	0.038	14.3	4.21	4.21
Dry matter (40 - 105°C)	23374	0.99	-	0.022	8.5	2.33	2.33
2-16 µm texture	2401	0.96	-	0.181	4.7	3.27	3.28
Median sand (50 – 2000 µm)	2518	0.83	2017	-1.242	2.2	26.67	26.70
PLFA total	1093	0.88	2019	5.808	2.7	299.39	299.45
PLFA fungi	1077	0.84	2019	1.420	2.3	106.84	106.85
PLFA bacteria	1086	0.91	2019	3.837	3.0	108.68	108.74

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