

Combining Laser-Induced Breakdown Spectroscopy (LIBS) and Visible Near-Infrared Spectroscopy (Vis-NIRS) for Soil Phosphorus Determination

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Supplementary Material

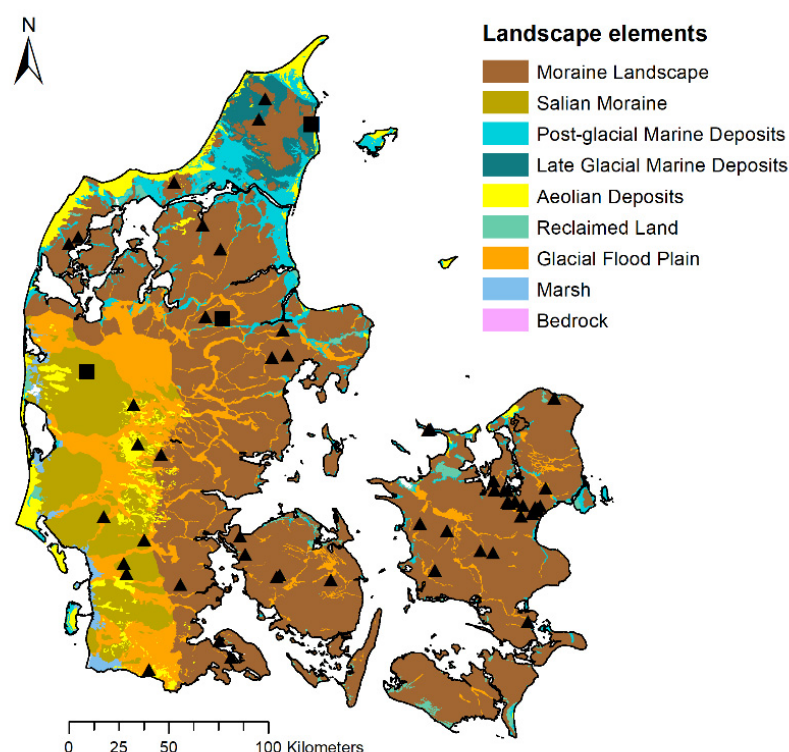


Figure S1. Location of the soil samples collected in Denmark. Triangles and squares indicate, respectively, the country-scale sample set (DK) and the sample sets from fields at Saeby (northern Jutland), Aarup (central Jutland) and Soervad (western Jutland). The underlying geological origin [S1] is shown as background.

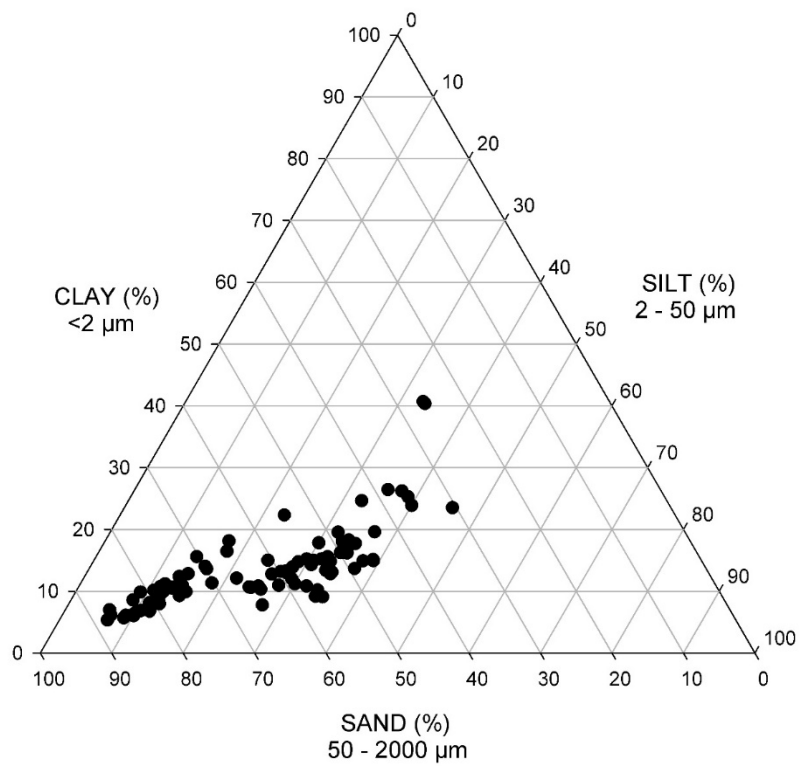


Figure S2. The USDA soil texture triangle.

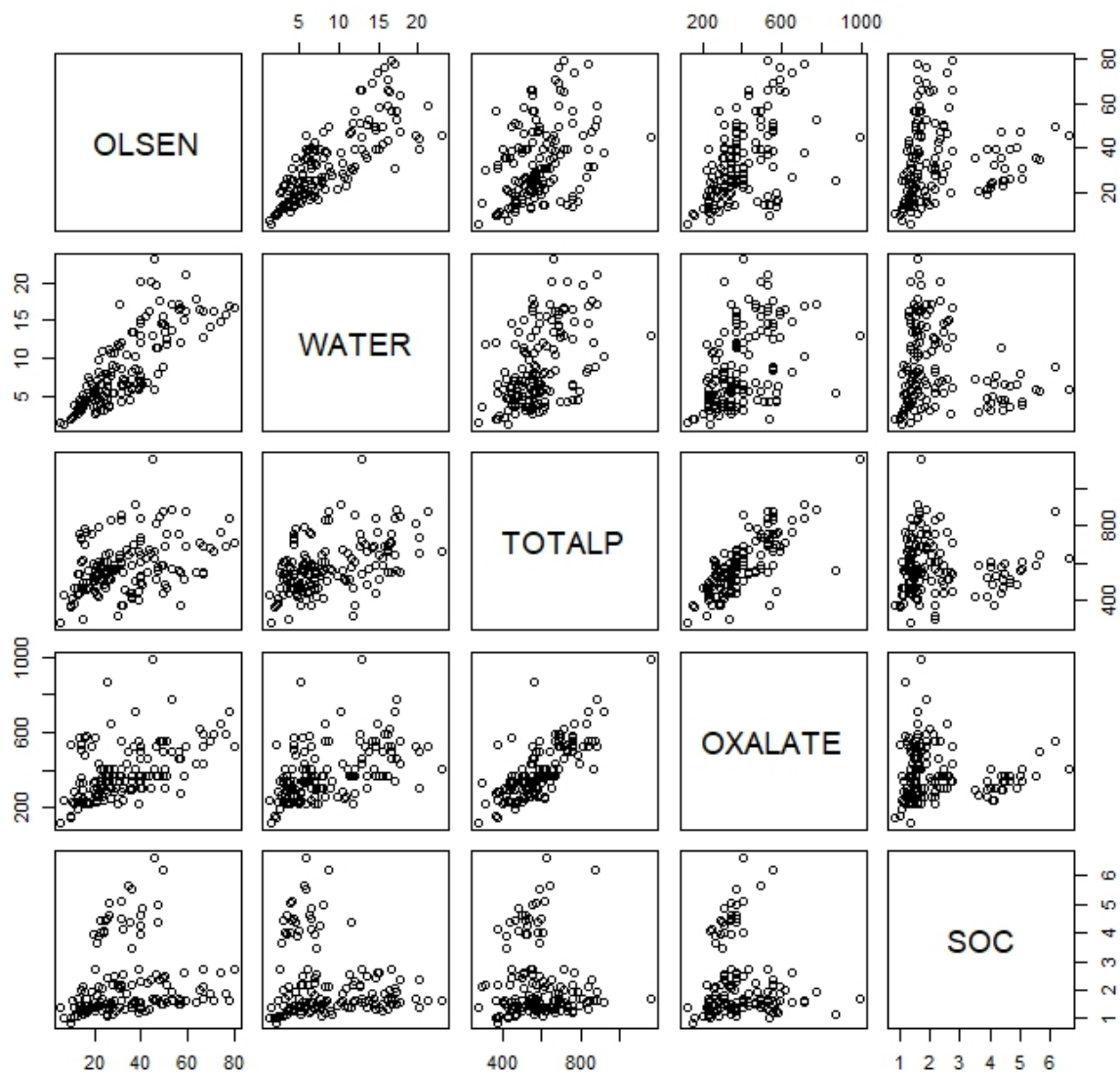


Figure S3. The linear relationship between SOC and the different P fractions; Olsen P (OLSEN) (mg kg^{-1}), Water-extractable P (WATER) (mg kg^{-1}), Total P (TOTAL) (mg kg^{-1}), Oxalate-extractable P (OXALATE) (mg kg^{-1}) and soil organic carbon (SOC) (g kg^{-1}).

Table S1. Partial least squares regression (10-fold cross-validation) results for LIBS soil phosphorus determination.

Phosphorus Ref Method	Variable Selection Method	NV ¹	RMSEC ²	R ²	RMSECV ³	Rcv ²	Bias ⁴	NF ⁵
P_{water}	None	2041	3.7	0.47	3.9	0.43	-0.01	4
	iPLS	80	3	0.66	3.2	0.62	-0.009	5
	CARS	16	2.4	0.78	2.6	0.73	0.012	8
P_{olsen}	None	2041	5.6	0.74	9.5	0.67	-0.06	10
	iPLS	180	7.9	0.78	8.8	0.73	-0.02	7
	CARS	18	6.8	0.83	7.6	0.79	0.012	7
P_{ox}	None	2041	70	0.74	81.7	0.64	-0.13	10
	iPLS	160	57.3	0.82	64.6	0.77	0.47	7
	CARS	25	44.6	0.89	50.1	0.86	1.6	8
TP	None	2041	123.2	0.23	131.7	0.12	-2.6	4
	iPLS	80	60	0.76	73	0.72	1.9	5
	CARS	25	73.6	0.73	84.8	0.64	0.95	7

¹ Number of variables (wavelengths); ² Root mean squared error of calibration; ³ Root mean squared error of cross-validation; ⁴ The difference of the mean of the predicted versus the mean of the reference values; ⁵ Number of factors or latent variables.

Table S2. Results of variable selection methods (iPLS and CARS) presented by the commonly selected wavelengths for the P pools and their elemental assignation.

Method	Number of Selected Variables (P _{water} , P _{olsen} , P _{ox} , TP) ¹	Commonly Selected Wavelengths in nm (P pool)	Corresponding Emission Line/ Molecular Bond/Soil Component	Reference
iPLS	80, 180, 160, 80	206.87 - 209.35, 212.09 - 214.58 (P _{olsen} , TP) 214.7 - 217.19 (P _{water} , P _{ox}) 372.7 - 374.9 (P _{olsen} , P _{ox})	P (I) Ca	Díaz et al., 2012 [28] Lu et al., 2013 [30] Vieira et al., 2018 [90] Huang et al., 2019 [84]
CARS	LIBS 16, 18, 25, 25	279.78, 280.43 (all P pools) 213.53 (P _{olsen} , P _{water} , P _{ox}) 214.18, 214.32, 216.01 (P _{olsen} , P _{ox} , TP) 213.66, 255.28 (P _{water} , P _{ox} , TP) 193.45, 294.97, 312.85, 313.11 (P _{olsen} , P _{water}) 213.14 (P _{ox} , TP) 324.76, 399.96, 400.07 (P _{water} , P _{ox})	Mg P (I) C	Essington et al., 2009 [S2] Yu et al., 2016 [S3] Díaz et al., 2012 [28] Lu et al., 2013 [30] Vieira et al., 2018 [90] Nicolodelli et al., 2014 [S4]
iPLS	116, 315, 219, 232	604.5 - 614.5, 814.5 - 824.5 (P _{water} , P _{olsen}) 1942-1952, 2110 - 2120 (P _{ox} , TP) 2309.5 - 2319.5 (P _{olsen} , P _{ox})	Fe-oxides and functional groups of SOC O-H and possibly N-H bonds	Stenberg et al., 2010 [43] Clark et al. 1999 [44]
CARS	Vis-NIRS 93, 40, 26, 63	413.5 - 414, 419.5, 420.5 (P _{ox} , P _{water}) 414.5, 584 - 585.5 (P _{water} , TP) 2042.5 - 2043.5 (P _{olsen} , P _{water}) 2282,2315.5 (P _{olsen} , TP) 2496, 2496.5, 2497.5 (P _{ox} , TP) 2498 (P _{olsen} , P _{ox} , TP)	Fe-oxides and functional groups of SOC O-H and possibly N-H bonds	Stenberg et al., 2010 [43] Clark et al., 1999 [44]
iPLS	186, 403, 434, 155	212.6 - 216.5 (P _{olsen} , P _{ox} , TP) 655 - 670, 1615 - 1630 (P _{olsen} , TP), 2312.5 - 2327.5 (P _{olsen} , P _{ox})	P (I) Fe-oxides and functional groups of SOC O-H bonds	Díaz et al., 2012 [28] Lu et al., 2013 [30] Vieira et al., 2018 [90] Stenberg et al., 2010 [43] Clark, 1999 [44]
CARS	LIBS-vis- NIRS 86, 132, 90, 80	213.5-213.8, 214.9, 302, 602.5-604 (all P pools) 198.9, 253.5, 416.5, 421.5-422, 2459 -2460 (P _{olsen} , P _{water} and P _{ox}) 185.9 -186, 279.9 -280 (P _{olsen} , P _{water} and TP) 215.1, 2464 - 2465.5 (P _{olsen} , P _{ox} , TP)	P (I) Fe (I) 301.8 Mg Fe-oxides and functional groups of SOC O-H bonds	Díaz et al., 2012 [28] Lu et al., 2013 [30] Vieira et al., 2018 [90] Essington et al., 2009 [S2] Yu et al., 2016 [S3] Stenberg et al., 2010 [43] Clark et al., 1999 [44]

¹ P_{water}, P_{olsen}, P_{ox}, TP refer to water-extractable P, olsen P, oxalate-extractable P and total P.

Table S3. Partial least squares regression (10-fold cross-validation) results for vis-NIRS soil phosphorus determination.

Phosphorus Ref Method	Variable Selection Method	NV ¹	RMSEC ²	R ²	RMSECV ³	Rcv ²	Bias ⁴	NF ⁵
P_{water}	None	4165	3	0.65	3.3	0.6	-0.04	5
	iPLS	116	3.1	0.62	3.3	0.6	-0.04	5
	CARS	93	2.5	0.76	2.7	0.72	-0.02	12
P_{olsen}	None	4165	10.5	0.6	11.1	0.56	-0.05	4
	iPLS	315	6.3	0.85	8.3	0.75	0.02	15
	CARS	40	7.9	0.78	9.0	0.71	-0.16	12
P_{ox}	None	4165	89	0.6	101	0.5	-0.21	7
	iPLS	210	87.2	0.62	96.2	0.54	-0.34	9
	CARS	26	70	0.7	76.3	0.64	0.2	9
TP	None	4165	110.4	0.38	119	0.28	0.61	4
	iPLS	232	94.2	0.55	103.2	0.46	0.54	9
	CARS	63	84.1	0.64	95.3	0.54	0.29	11

¹ Number of variables (wavelengths); ² Root mean squared error of calibration; ³ Root mean squared error of cross-validation; ⁴ The difference of the mean of the predicted versus the mean of the reference values; ⁵ Number of factors or latent variables.

Table S4. Partial least squares regression (10-fold cross-validation) results for LIBS-vis-NIR soil phosphorus determination.

Phosphorus Ref Method	Variable Selection Method	NV ¹	RMSEC ²	R ²	RMSECV ³	Rcv ²	Bias ⁴	NF ⁵
P_{water}	None	6204	3.3	0.58	3.7	0.51	-0.035	4
	iPLS	186	2.2	0.82	2.5	0.76	0.05	10
	CARS	86	1.8	0.88	2.2	0.82	0.03	11
P_{olsen}	None	6204	10.5	0.60	11.4	0.53	-0.11	6
	iPLS	403	5.8	0.88	6.7	0.84	0.0036	10
	CARS	132	5.7	0.88	6.8	0.83	0.07	11
P_{ox}	None	6204	84.5	0.64	104.2	0.46	-0.73	10
	iPLS	434	46.5	0.88	53.6	0.85	-0.74	8
	CARS	90	43.8	0.90	51.2	0.86	-2.5	9
TP	None	6204	103.5	0.45	115.8	0.40	0.60	7
	iPLS	155	70.3	0.74	87.2	0.60	-2.9	10
	CARS	80	50.5	0.86	58.4	0.82	-0.28	10

¹ Number of variables (wavelengths); ² Root mean squared error of calibration; ³ Root mean squared error of cross-validation; ⁴ The difference of the mean of the predicted versus the mean of the reference values; ⁵ Number of factors or latent variables.

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