Supplementary Information (SI) for Analytical Methods.
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Supplementary materials

Rapid quality assessment of organic fertilizers using fused FTIR and LIBS spectroscopy with machine learning

Xuebin Xu [a, b], Fei Ma [a], Jianmin Zhou [a] and Changwen Du [a, b, †]

[a] *The State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 211135 (China)*

b *College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100049 (China)*

[†] Corresponding author.

E-mail address: chwdu@issas.ac.cn

Tel: +86-25-86881565

Fax: +86-2586881000

Table S1 Geographic distribution of samples.

Region	Number of samples
Inner Mongolia	132
Zhejiang	4
Anhui	4
Jilin	1
Henan	2
Tianjing	1
Hainan	1
Jiangsu	5
Liaoning	1
Heilongjiang	1
Fujian	1
Beijing	1
Shaanxi	1
Shandong	2
Hunan	27
Hubei	18
Jiangxi	37
Hebei	2
Guangxi	34
Gansu	58

Table S2 The properties of the selected samples for two-dimensional correlation spectral (2DCOS) analysis.

Disturbance	Type	pH	OC (%)	N (%)	P (%)	K (%)
OC	Uncomposted	8.21	42.19	2.27	0.55	0.63
		8.46	33.58	1.85	0.47	0.58
		8.69	19.30	1.68	0.56	0.72
	Composted	9.73	7.91	0.69	0.21	1.03
		6.39	40.07	0.54	0.02	0.25
		5.94	31.92	4.18	0.69	0.82
		7.29	19.93	1.76	0.37	0.83
		7.51	7.47	0.67	0.25	0.85
K	Uncomposted	8.16	27.21	2.70	1.37	3.79
		6.36	29.02	3.05	1.77	2.32
		8.13	29.92	3.14	1.89	1.22
	Composted	8.78	31.73	2.65	0.82	0.38
		6.84	19.99	3.15	1.35	8.21
		7.19	19.60	1.77	1.68	3.74
		6.68	17.79	3.82	1.11	1.29
		6.61	21.11	0.45	1.27	0.23

Table S3 The positive and negative values of synchronous and asynchronous FTIR cross-peaks under OC perturbation.

Position	Uncomposted				Composted		
	Syn	Asyn	Sequence		Syn	Asyn	Sequence
(~3600, ~1550)	+	+	3600→1550				
(~3600, ~1000)	−	+	1000→3600				
(~3200, ~2800)	+	−	2800→3200		+	−	2800→3200
(~3200, ~1550)	+	−	1550→3200		+	−	1550→3200
(~3200, ~1000)	−	+	1000→3200		+	−	1000→3200
(~3000, ~1550)	+	−	1550→3000		+	−	1550→3000
(~3000, ~1000)	−	+	1000→3000		+	−	1000→3000
(~1550, ~1000)	−	+	1000→1550		+	−	1000→1550
1000→3600→1550→3200, 1000→3600→1550→3000, 2800→3200					1000→1550→3200, 1000→1550→3000, 2800→3200		

Table S4 The positive and negative values of synchronous and asynchronous FTIR cross-peaks under K perturbation.

Position	Uncomposted				Composted		
	Syn	Asyn	Sequence		Syn	Asyn	Sequence
(~3200, ~1550)	+	−	1500→3200				
(~3200, ~1000)	+	−	1000→3200				
(~3000, ~1550)	+	+	3000→1500				
(~1550, ~1000)	+	+	1500→1000				
3000→1550→1000→3200							

Table S5 Comparative analysis of time and efficiency between standard wet chemistry methods and the proposed portable FTIR-LIBS framework for multi-parameter (pH, OC, N, P, K) assessment.

Analytical step	SWCM	FTIR-LIBS Framework	Notes / Implications
Sample preparation	Required (drying, grinding)	Required (drying, grinding)	Common and necessary step for both methods.
Sample digestion/preparation	Required (hours, uses hazardous chemicals)	Required (pelletizing for LIBS, ~5 min; none for FTIR)	FTIR-LIBS avoids hazardous digestions. Pelletizing is rapid and safe.
Measurement time per sample	Hours to over a day (sequential tests)	~10 minutes total (FTIR: ~1 min; LIBS: ~5-7 min)	Dramatic reduction in analysis time. Enables high-throughput.
Consumables & reagents	Significant (acids, oxidants, standards)	Minimal (pellitizing cup, argon gas)	FTIR-LIBS drastically reduces recurring costs and chemical waste.
Labor skill level	High (requires trained chemists)	Moderate (training on operation and software)	Makes analysis accessible to a wider range of technicians.
Environmental impact	High (generates chemical waste)	Low (minimal waste generation)	FTIR-LIBS is a "greener" analytical technique.
Primary cost driver	Recurring cost of reagents and labor	Initial capital investment in instruments	FTIR-LIBS offers long-term cost efficiency and speed.

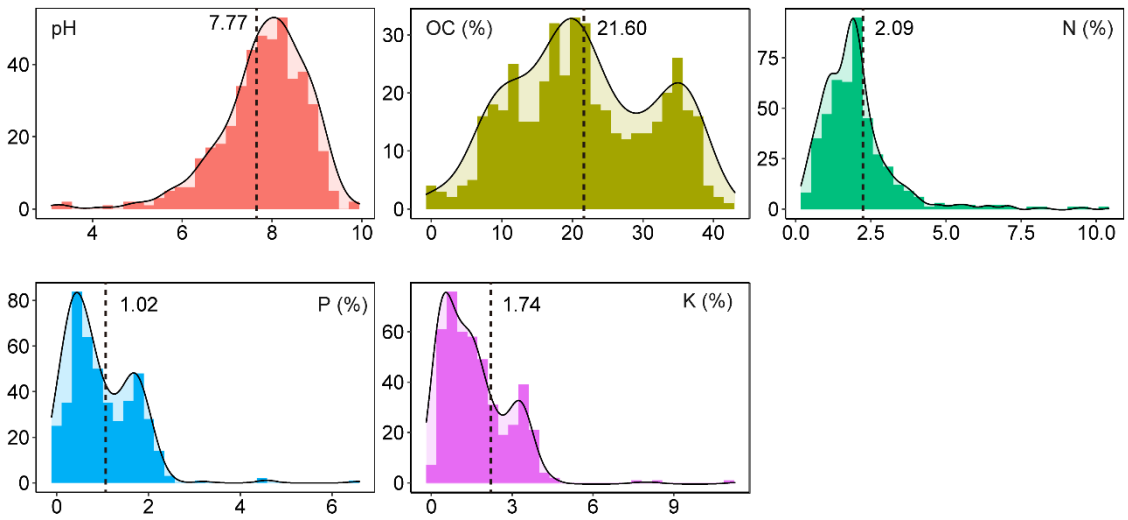

Fig. S1. The distributions of pH, OC, N, P, and K of organic fertilizers (N=453).

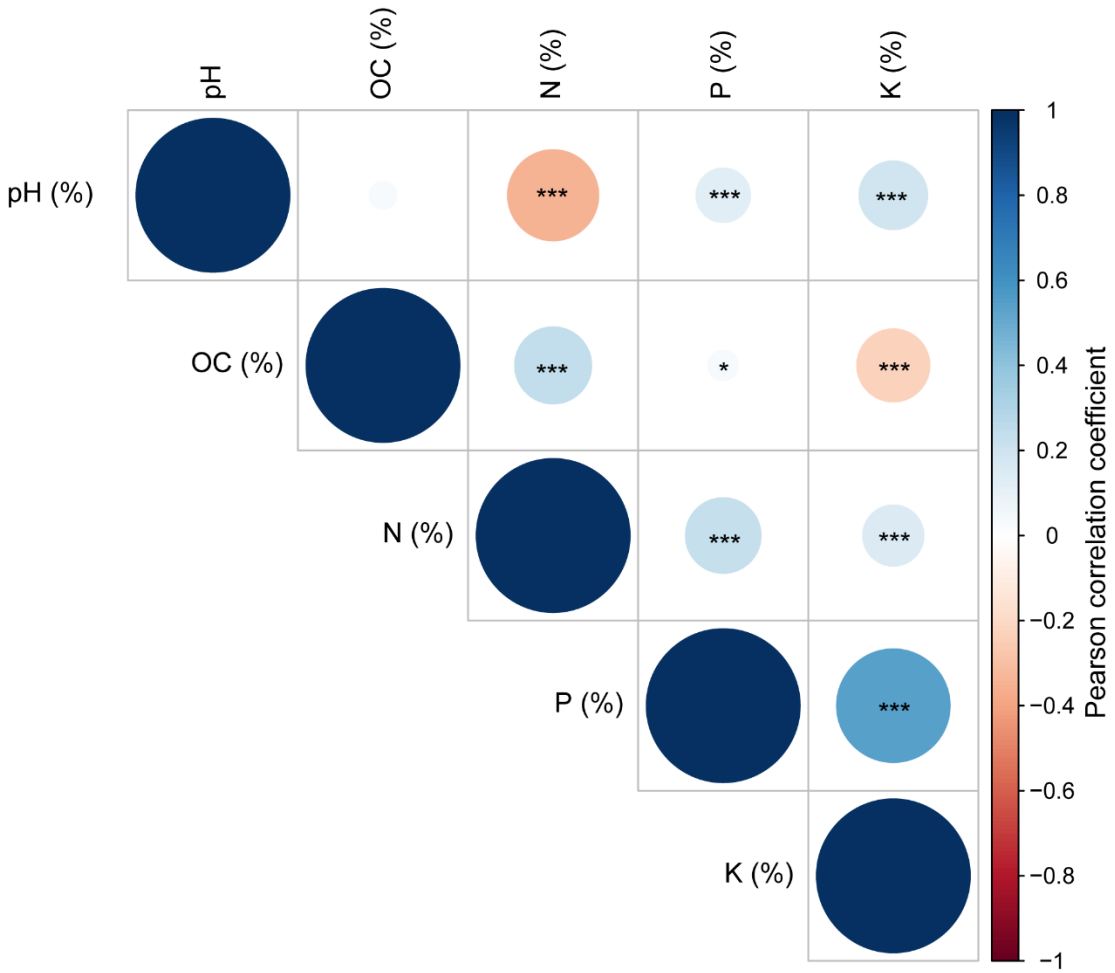

Fig. S2. Pearson correlations between pH, OC, N, P, and K of organic fertilizer (N=453). * and *** indicate significant correlation at $P < 0.05$ and $P < 0.001$, respectively.

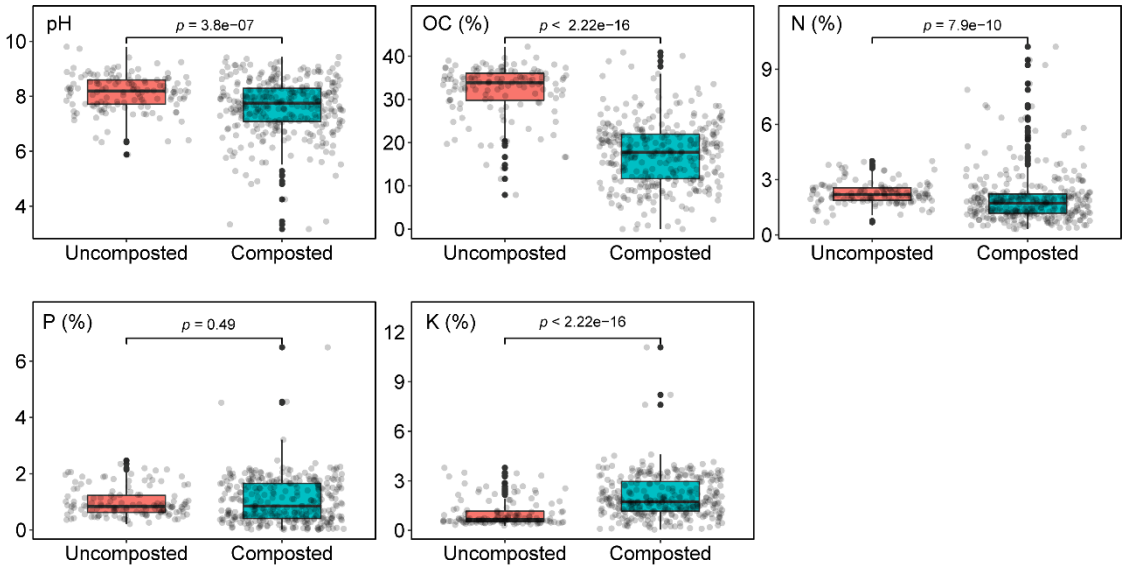

Fig. S3. Comparison of pH, OC, N, P, and K in uncomposted and composted organic fertilizers, respectively.

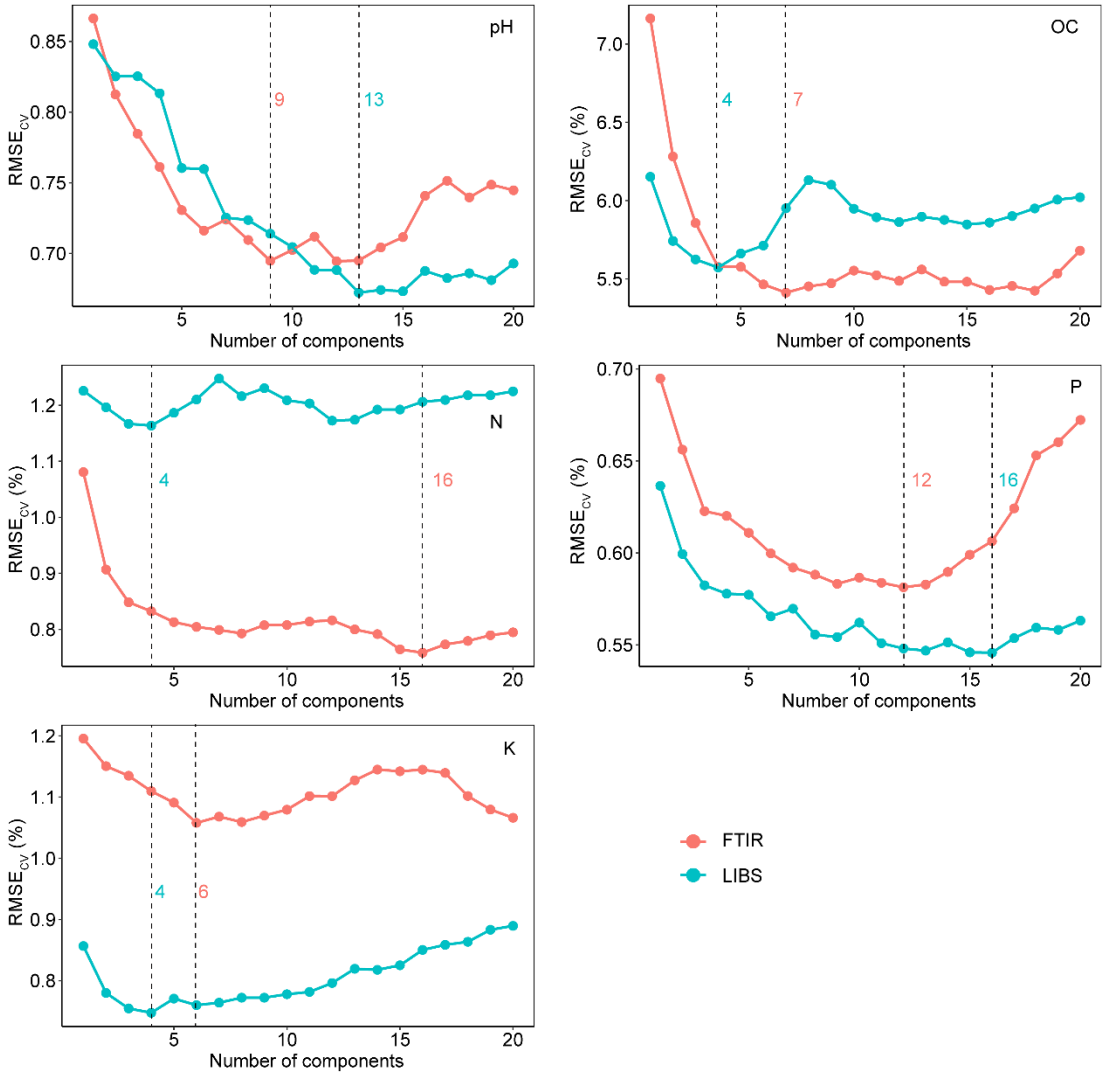

Fig. S4. Optimization of the parameter in partial least square (PLS) model according to 5-fold cross-validation.

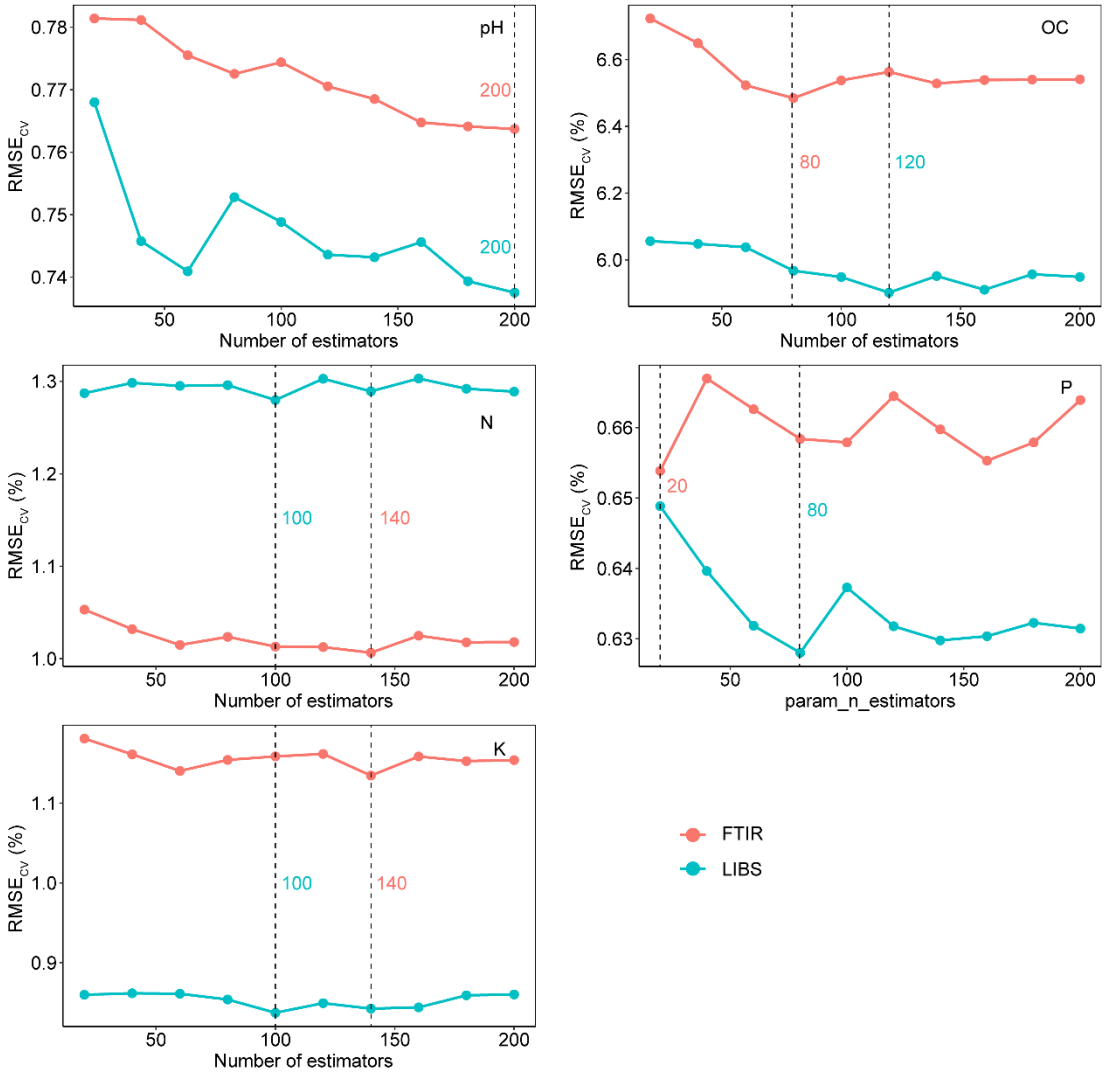

Fig. S5. Optimization of the parameter in random forest (RF) model according to 5-fold cross-validation.

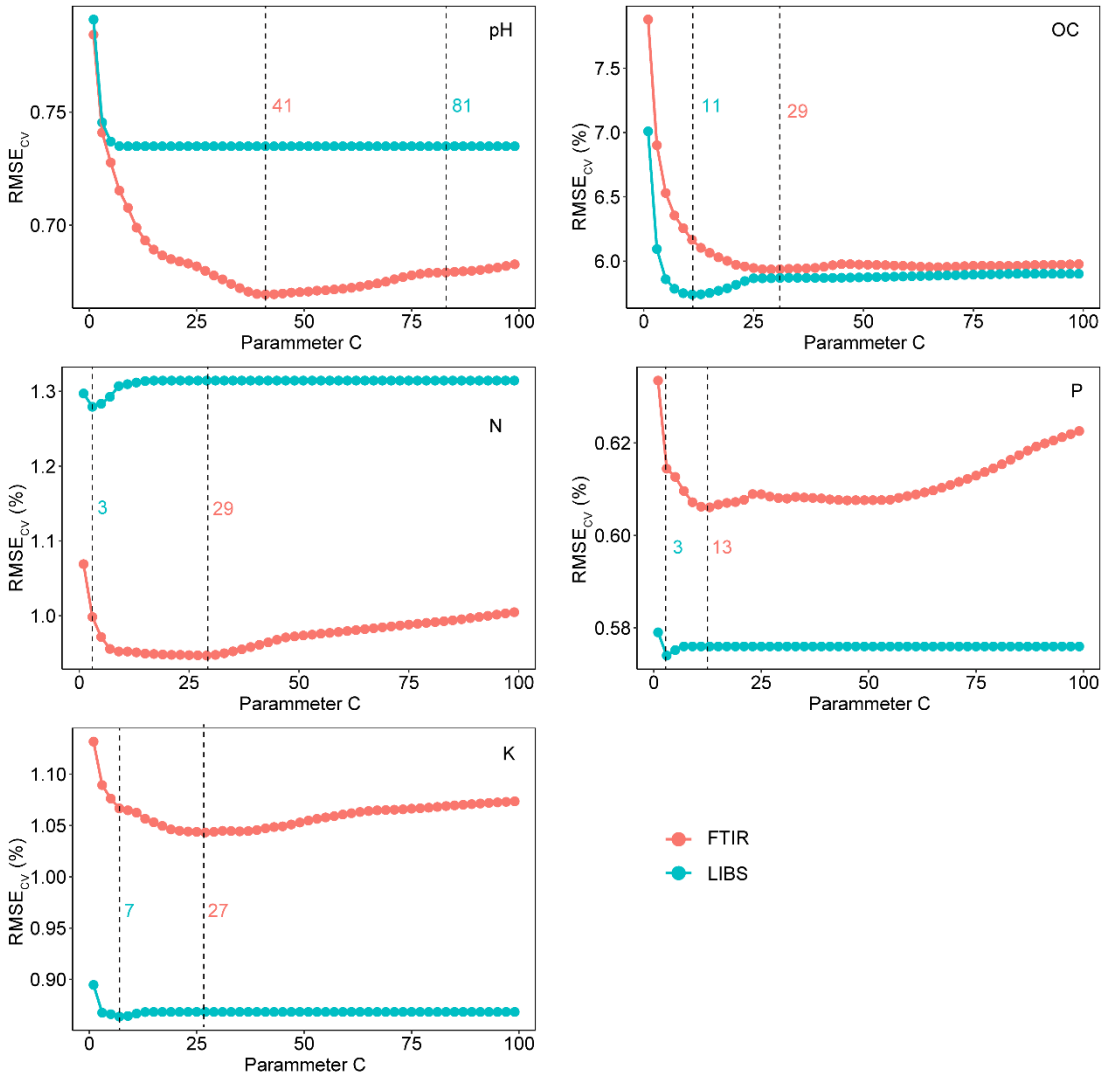

Fig. S6. Optimization of the parameter in support vector regression (SVR) model according to 5-fold cross-validation.

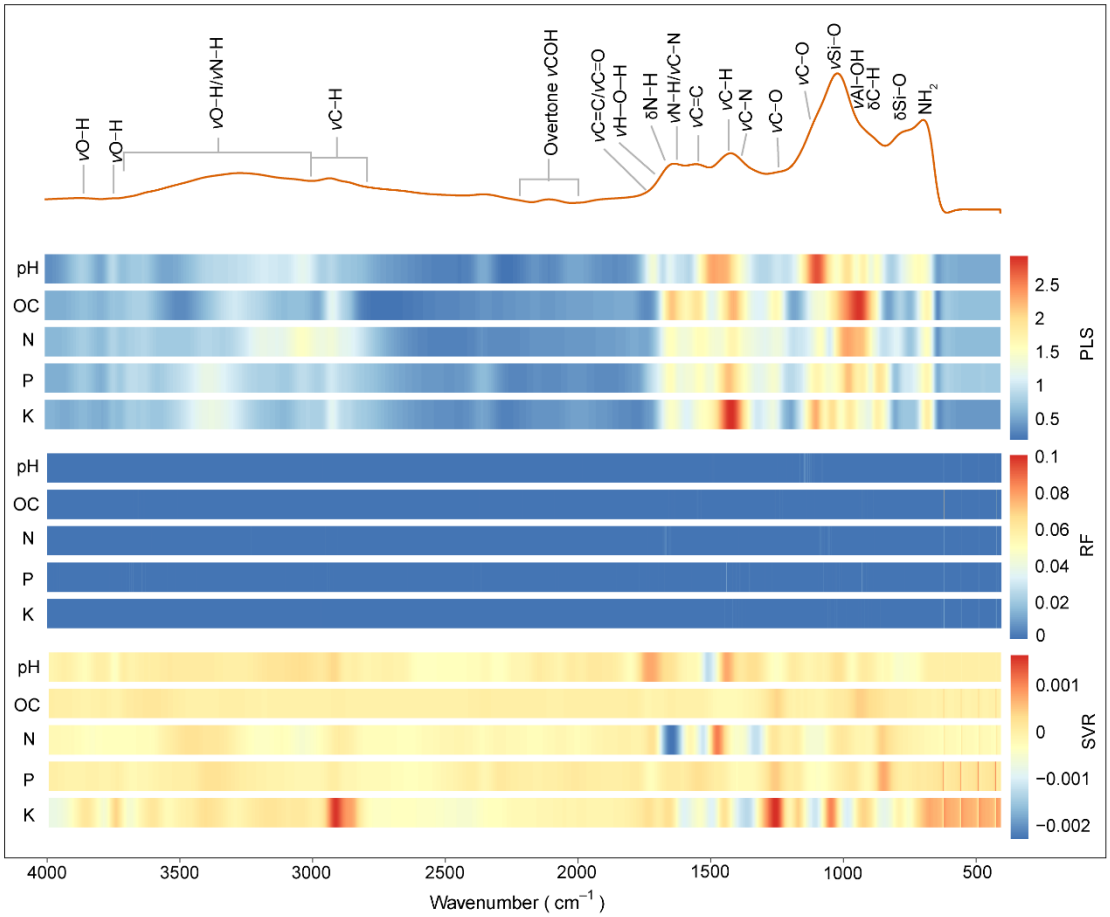

Fig. S7 Variable importance for predictions of pH, OC, N, P, and K based on FTIR spectra.

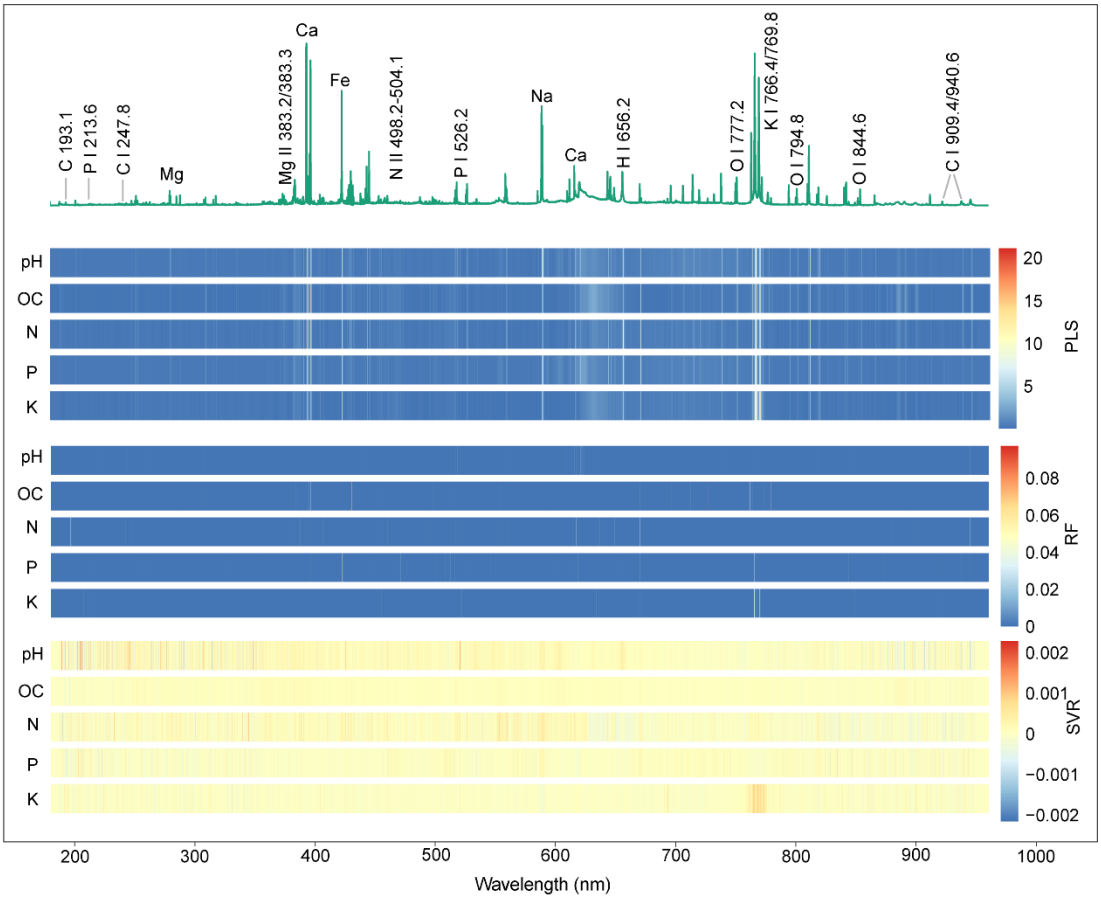

Fig. S8. Variable importance for predictions of pH, OC, N, P, and K based on LIBS spectra.

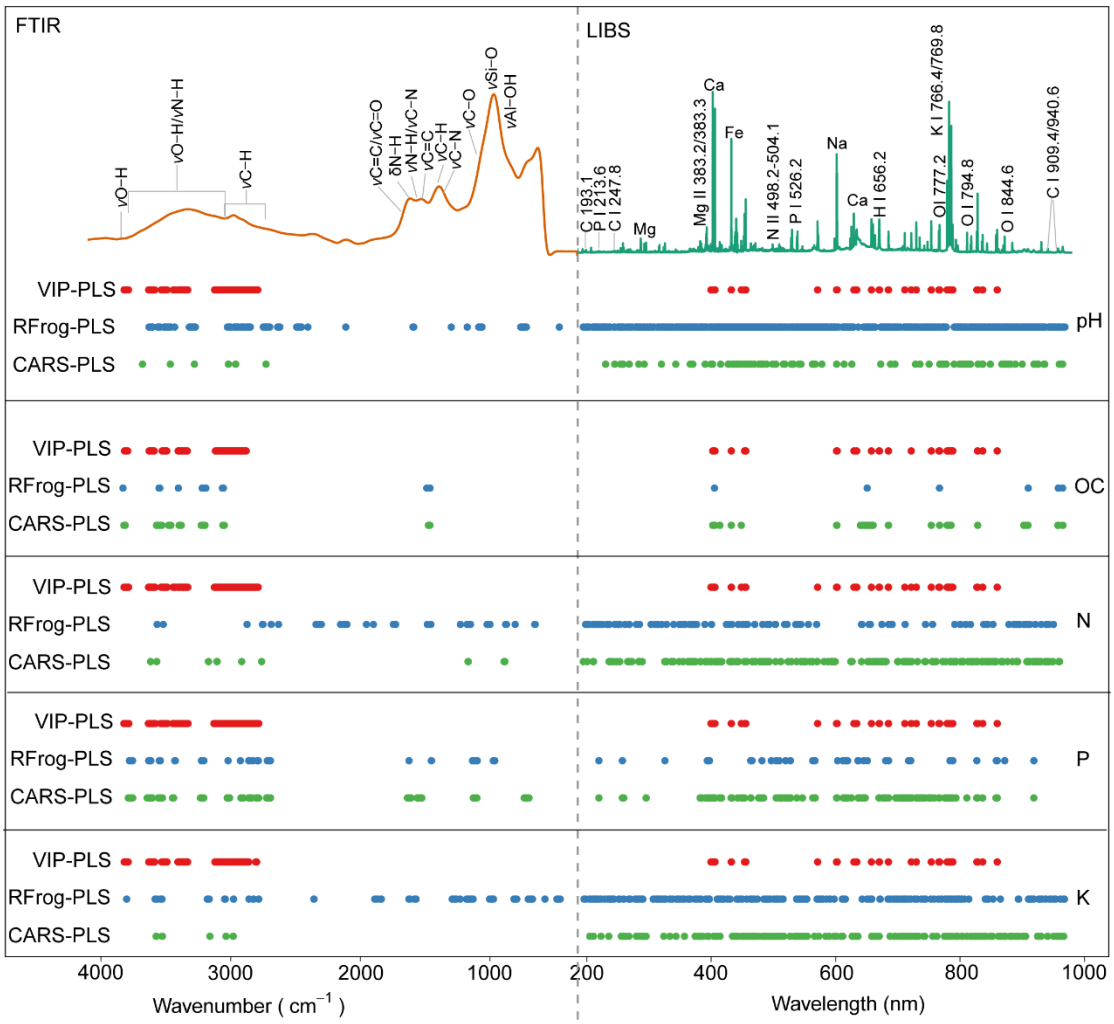

Fig. S9. Selected variables for predictions of pH, OC, N, P, and K by different variable selection models based on the fusion spectra of FTIR and LIBS.