EGU General Assembly 2020

Online | 4–8 May 2020

Biological sources and molecular composition of iron oxides bound organic carbon in agricultural soils

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Introduction

- Soil is the largest carbon pool in terrestrial ecosystem on Earth - larger than the total of atmosphere and aboveground biomass.
- Understanding the mechanisms for the storage and stability of soil organic carbon has drawn increasing attention.
- Possible mechanisms for SOC stabilization:

  Recalcitrance; Accessibility and Organo-mineral interactions
- The stability of SOC is largely due to the complex interactions between organic C and soil minerals (Han *et al*., 2016; Yu *et al*., 2017)

Introduction

- Due to their large surface area and high adsorption affinity, Fe oxides in soils play an important role in preserving OC (Chen *et al*., 2014; Ma *et al*., 2018).

- Recent quantitative characterization indicated the percentages of Fe-bound OC in a variety of settings:
  - 21.5±8.6%, marine sediments (Lalonde et al., 2012)
  - 15%, Wax Lake Delta sediments, USA (Shields et al., 2016)
  - 19.5±12.3%, forest soils, USA (Zhao et al., 2016)
  - 37.8%, permafrost soil, Qinghai-Tibet Plateau (Mu et al., 2016)

Introduction

- Limited information is available regarding the association of Fe-bound OC in arable soils.
- Due to cultivation and fertilization, OC in arable soils may change over a comparatively short time.
- Quantitative investigation on the binding of OC by iron oxides in agricultural soils is of pivotal importance for predicting global C cycle.

Objectives

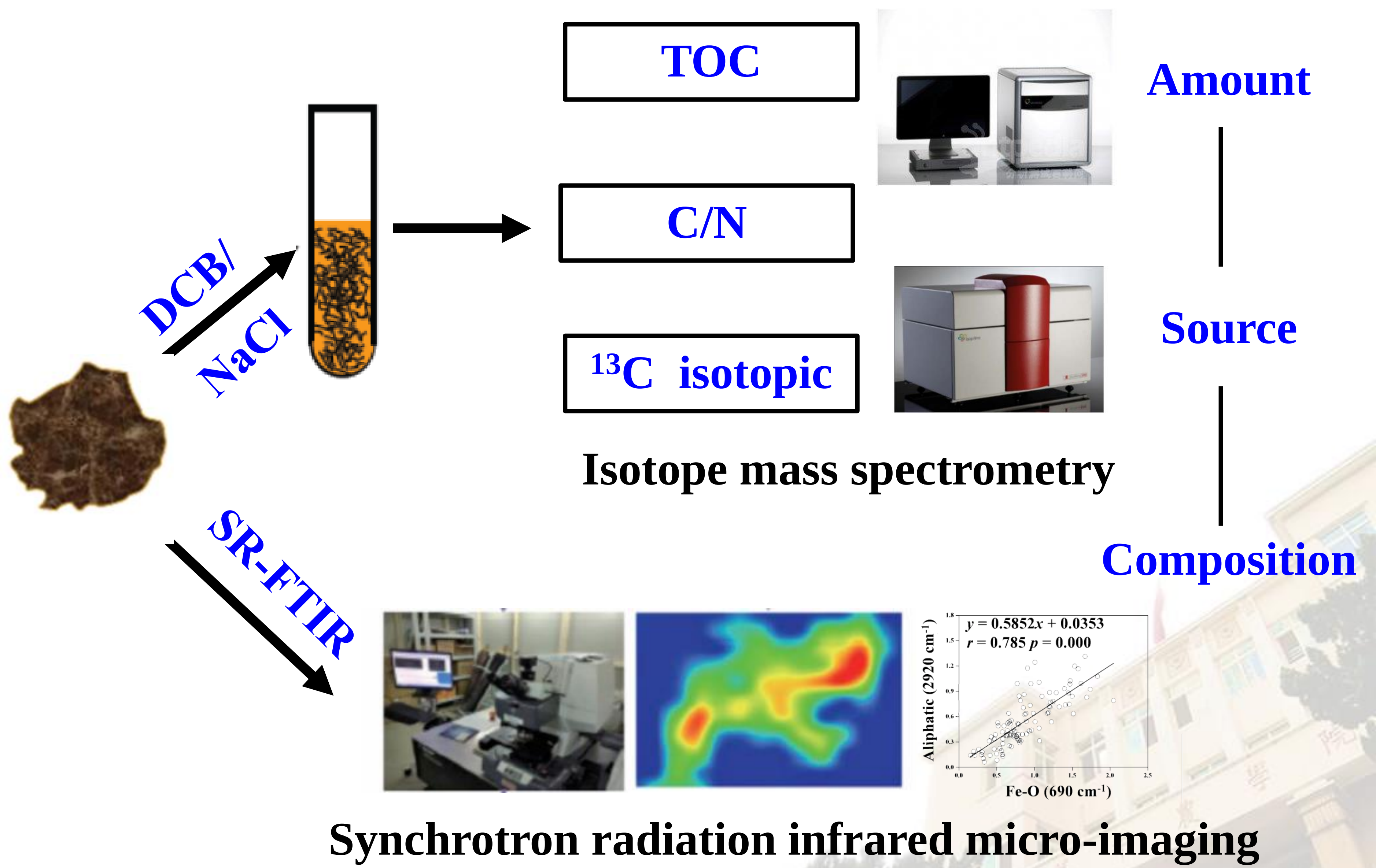
- Amount of OC trapped by Fe oxides in arable soils.
- Composition and possible sources of Fe-bound OC.

Material & Methods

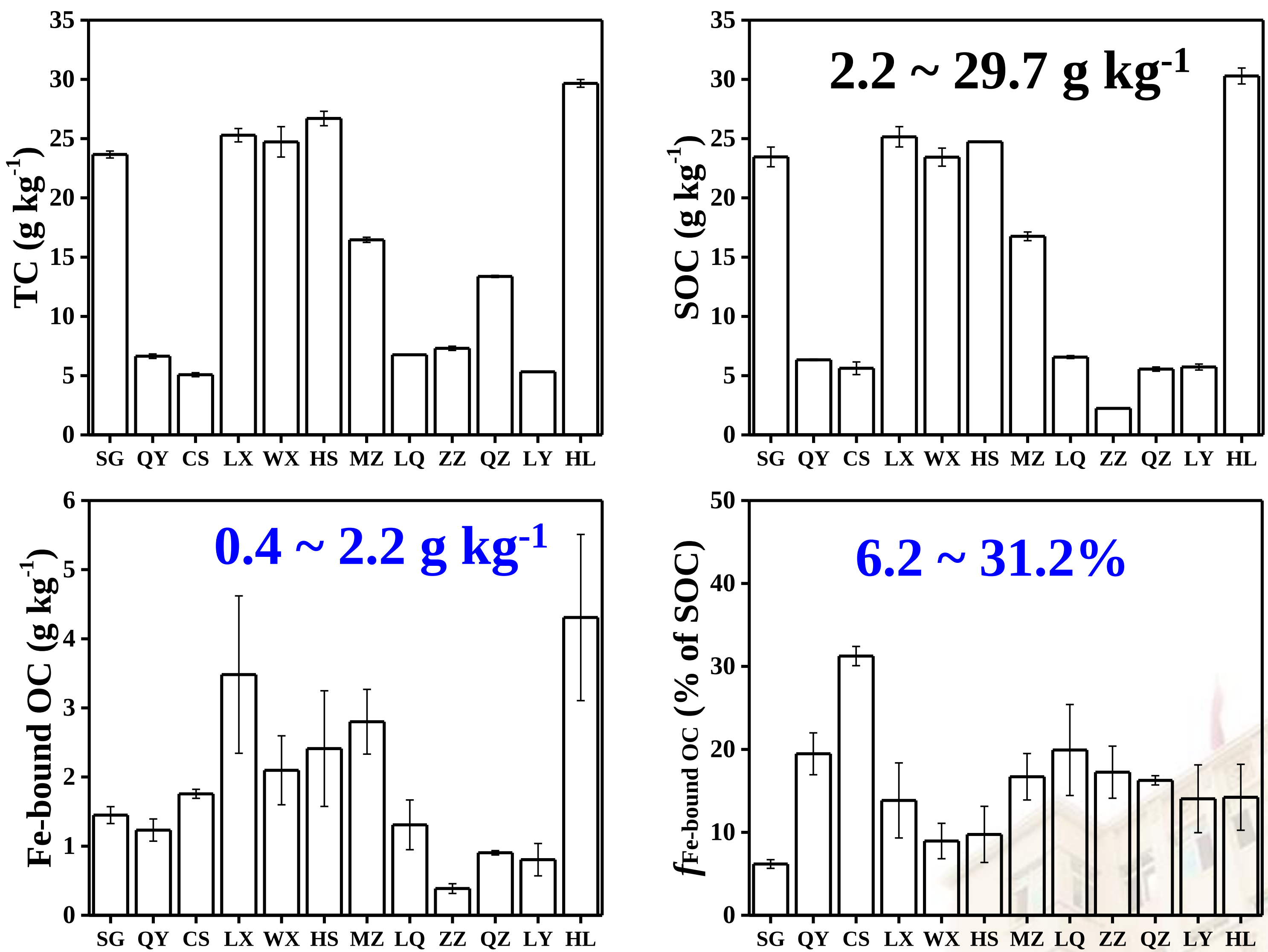
Soil samples (12 sites)

Location	Soil type	Soil order	Latitude N	Longitude E	Crop cultivation	Sampling time
SG	Red soil	Acrisols	25.05	113.65	Rice	Mar 2015
QY	Red soil	Acrisols	26.75	111.87	Corn–wheat	Nov 2015
CS	Red soil	Acrisols	28.55	113.32	Corn–sweet potato	Aug 2015
LX	Paddy soil	Anthrosols	29.39	113.25	Rice	Aug 2015
WX	Paddy soil	Anthrosols	29.85	115.55	Rapeseed–rice	Nov 2015
HS	Yellow-brown soil	Luvisols	30.10			
MZ	Paddy soil	Anthrosols	31.25			
LQ	Lime concretion black soil	Cambisols	32.92			
ZZ	Cinnamon soil	Cambisols	34.88			
QZ	Calcareous fluvo-aquic soil	Cambisols	36.87			
LY	Fluvo-aquic soil	Cambisols	36.90			
HL	Black soil	Phaeozems	47.43			

Material & Methods

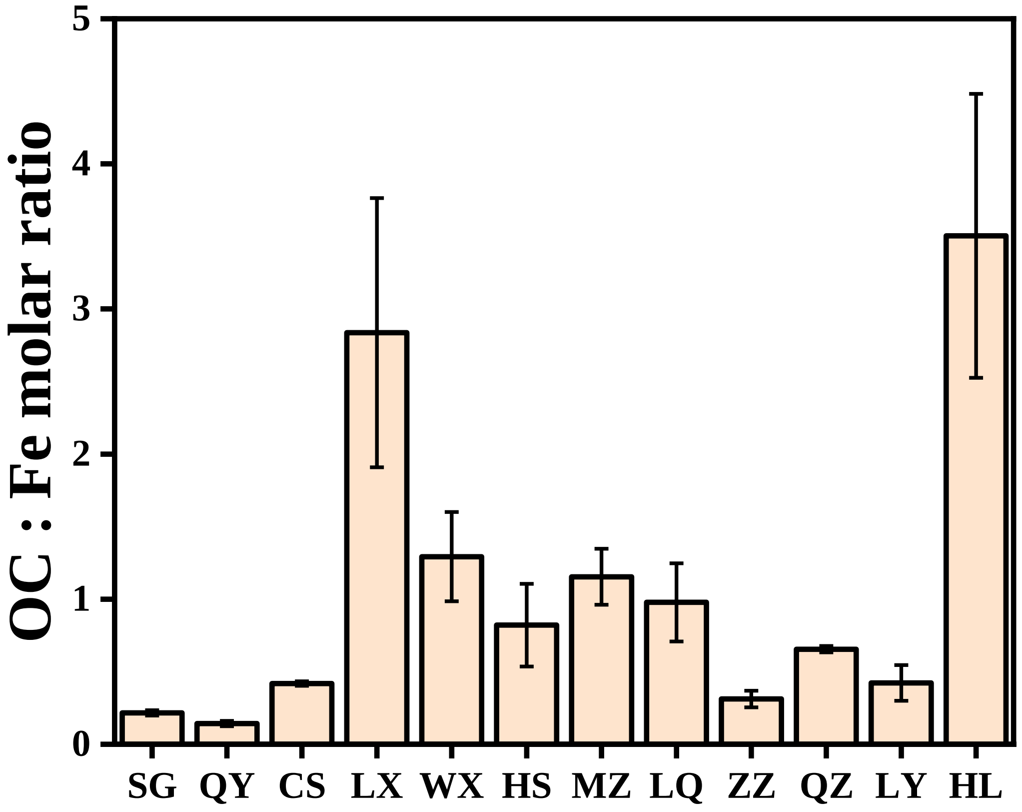


Results



TC, SOC, Fe-bound OC, and percent of Fe-bound OC/SOC ($f_{\text{Fe-bound OC}}$)

Results

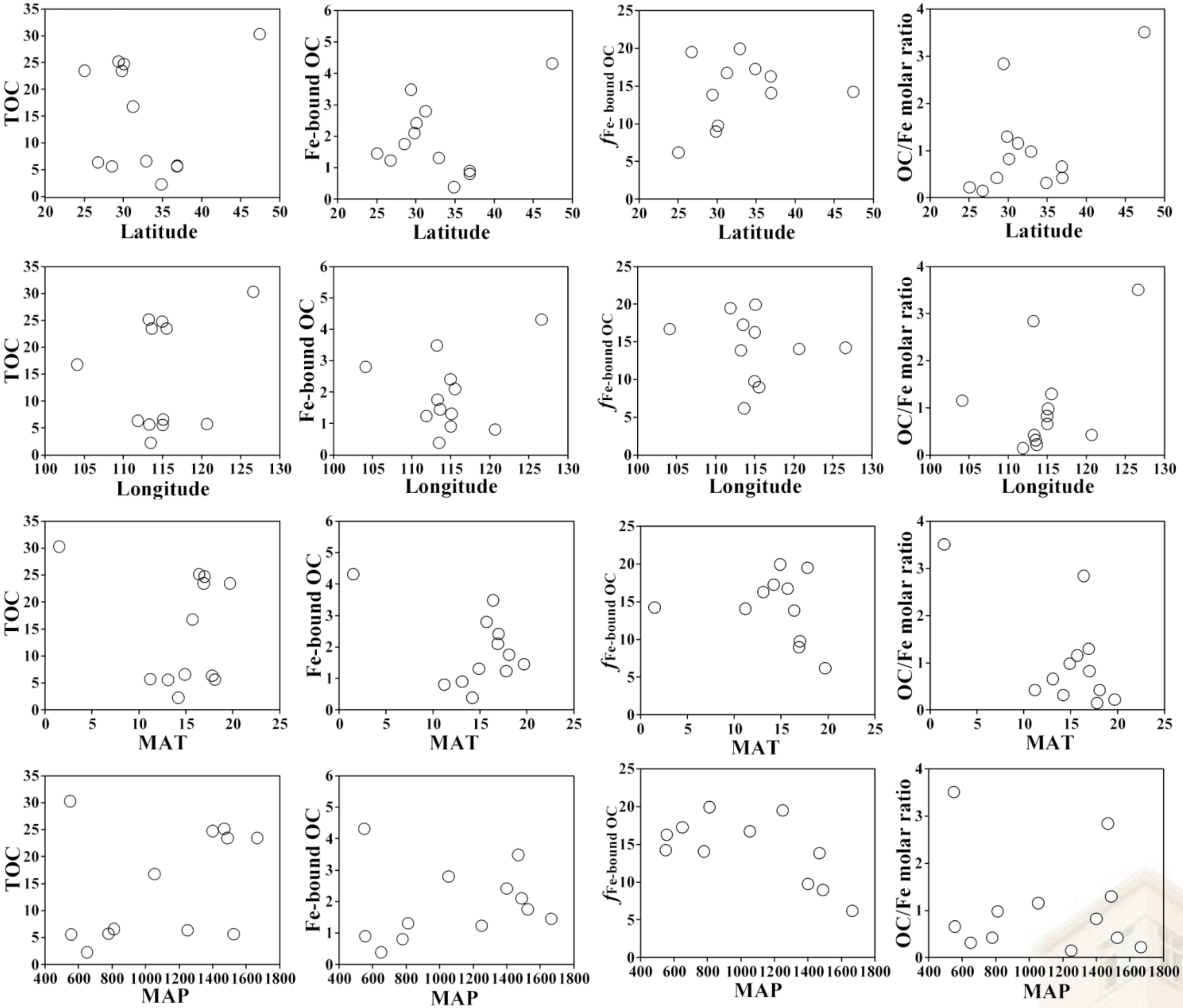


Molar ratios of OC/Fe

OC/Fe:
< 1 Adsorption
> 6 Coprecipitation

(Wang *et al*., *Nat. Commun.* 2017)

- The binding of OC with Fe oxides may vary from adsorption in most soils to coprecipitation in those with high contents of SOC.



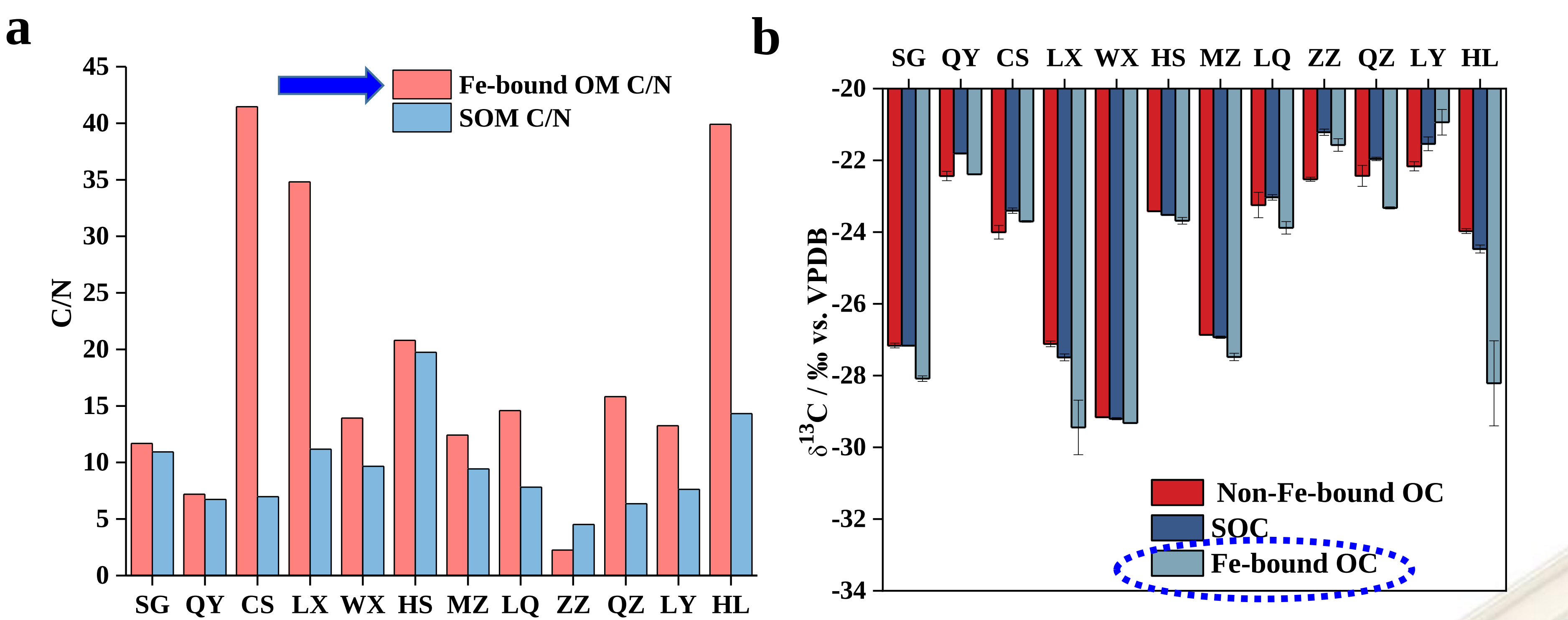
No clear variations were found with sampling sites

Relations among SOC, Fe-bound OC and environmental factors

Pearson correlation matrix for Fe-bound OC and soil properties

	Fe-bound OC	$f_{\text{Fe-bound OC}}$	OC:Fe
pH	-0.466	0.015	-0.300
SOC	**0.824****	**-0.633***	**0.689***
Fe_d	-0.237	0.063	-0.497
Fe_o	0.422	-0.458	0.123
Fe_p	0.310	-0.437	0.257
Fe_o/Fe_d	**0.707***	-0.351	**0.702***
Clay	-0.165	0.008	-0.339
Silt	0.505	-0.032	0.423
Sand	-0.428	0.028	-0.299
Fe-bound OC	1	-0.165	0.892
$f_{\text{Fe-bound OC}}$	-0.165	1	-0.174
OC:Fe	**0.892****	-0.174	1

- Fe-bound OC was mainly correlated with SOC and active Fe ratio.

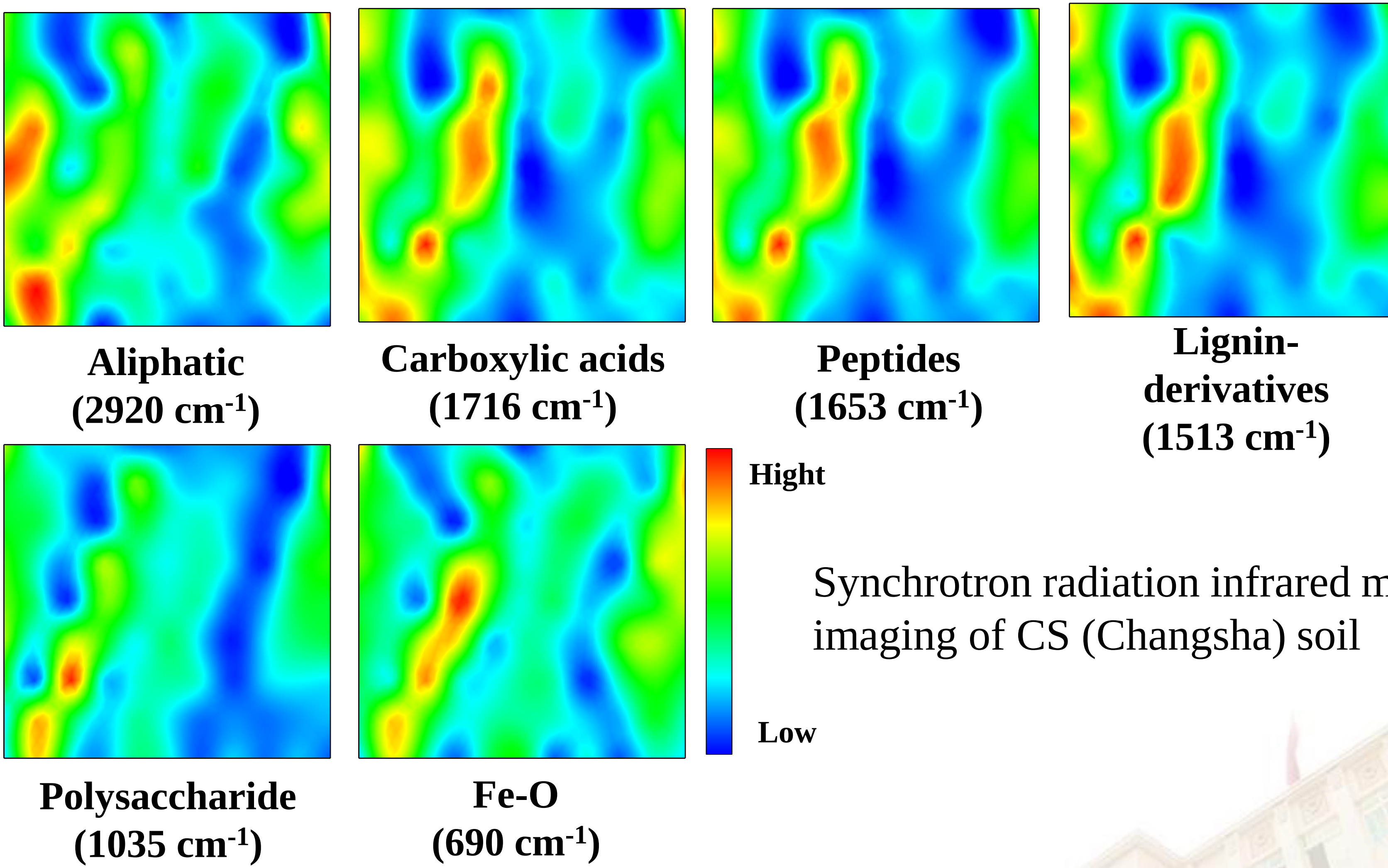


C/N ratio of Fe-bound OM and SOM (**a**), and $\delta^{13}C$ values of SOC and Fe-bound OC (**b**)

- Fe-bound OC had a larger C/N ratio than SOC.
- ^{13}C was relatively depleted in Fe-bound OC (0.99 ± 1.07‰, lighter) compared with SOC.

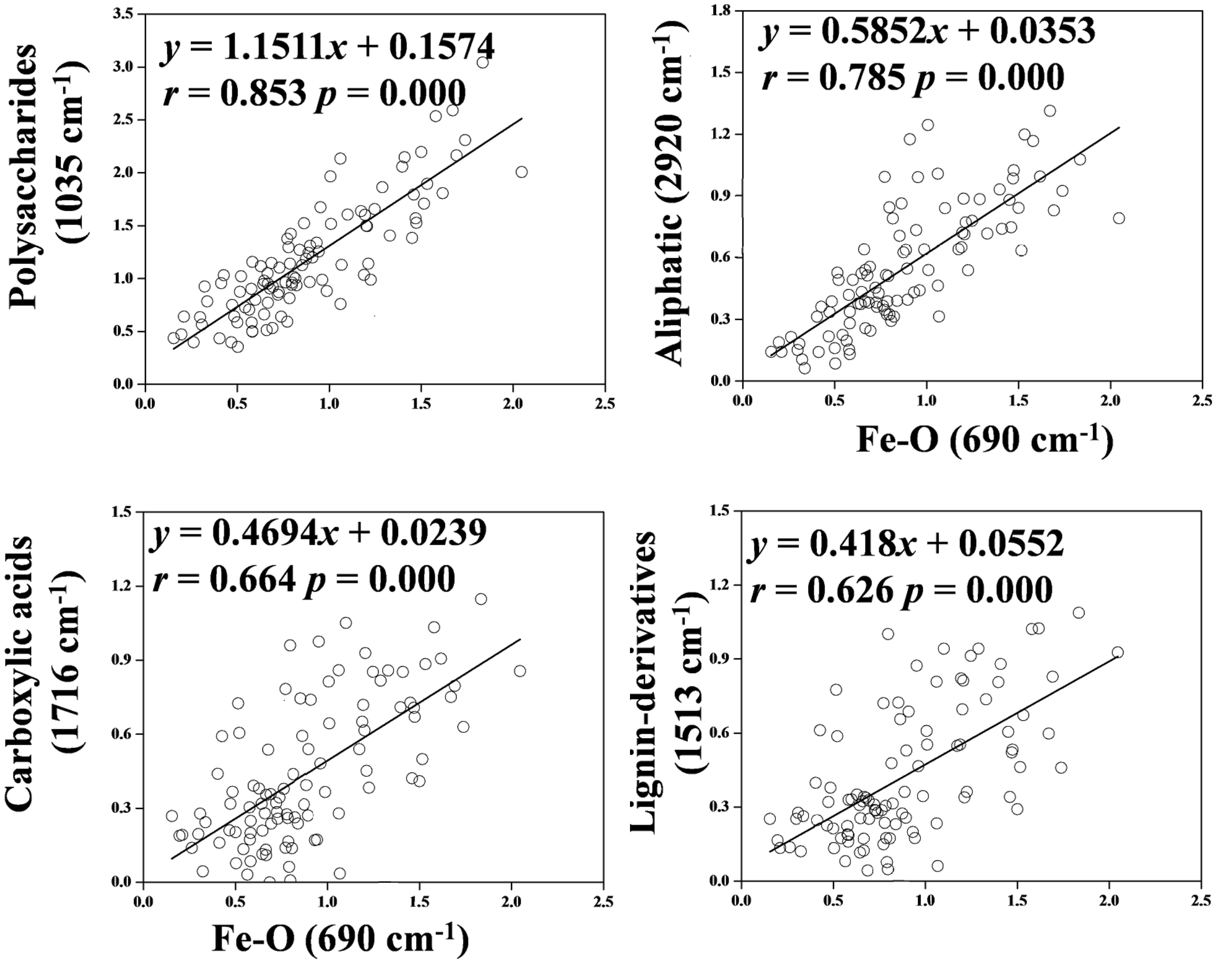
- It has been proposed that plant-derived SOM commonly has a larger C/N ratio than microbe-derived SOM (Schnecker *et al*., 2016; Six *et al*., 2001).
- The δ^{13}C values of OM usually increased with microbial transformation, whereas decreased with more plant inputs (Schnecker *et al*., 2016; Six *et al*., 2001; Taylor *et al*., 2003).

- The larger C/N ratio of Fe-bound OM and the relative depletion of ^{13}C in Fe-bound OC suggested that iron oxides preferentially bound plant-derived OC in arable soils.



Synchrotron radiation infrared micro-imaging of CS (Changsha) soil

- The spatial distribution of organic compounds was directly correlated with that of Fe-O



Correlations between the distribution of Fe-O and organic compounds (n = 99) in CS (Changsha) soil

- Correlation coefficient *(r)* : polysaccharides or aliphatic compounds > peptides > carboxylic acids > lignin derivatives

- The correlation coefficients (*r*) and regression slopes suggested that stronger associations occurred between Fe-O and polysaccharides or aliphatic compounds or peptides than carboxylic acids or lignin derivatives.
- Depletion of ^{13}C in Fe-bound OC indicated small percentage of peptides because proteins are usually ^{13}C-enriched (Zhao *et al.*, 2016)
- It is supposed that iron oxides preferentially stabilized polysaccharides and aliphatic compounds in arable soils.

Conclusions

- Approximately 6.2~31.2% (15.7±6.4%) of soil organic carbon is associated with iron oxides in cropland soils.
- The distribution of Fe-bound OC showed no clear variations in relation to sites.
- Iron oxides selectively stabilize plant-derived polysaccharides and aliphatic compounds.
- Results obtained would be helpful for the consideration of increasing C stabilization capacity and potential in agricultural soils.