Fluorescence spectroscopy: a sensitive tool for detecting changes in composition of water-extractable soil organic matter

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Dissolved organic matter (DOM)

Soil solutions contain a variety of organic compounds that play an active role in soil biogeochemical cycling and may be important indicators of microbial processes in general, and biodegradation processes in particular.

Identification and quantification of different pools of DOM may improve its sensitivity as an indicator for soil health and also may provide deeper understanding of the relations between this pool and bioprocesses.

EEM analysis and PARAFAC (Parallel Factors Analysis) modeling

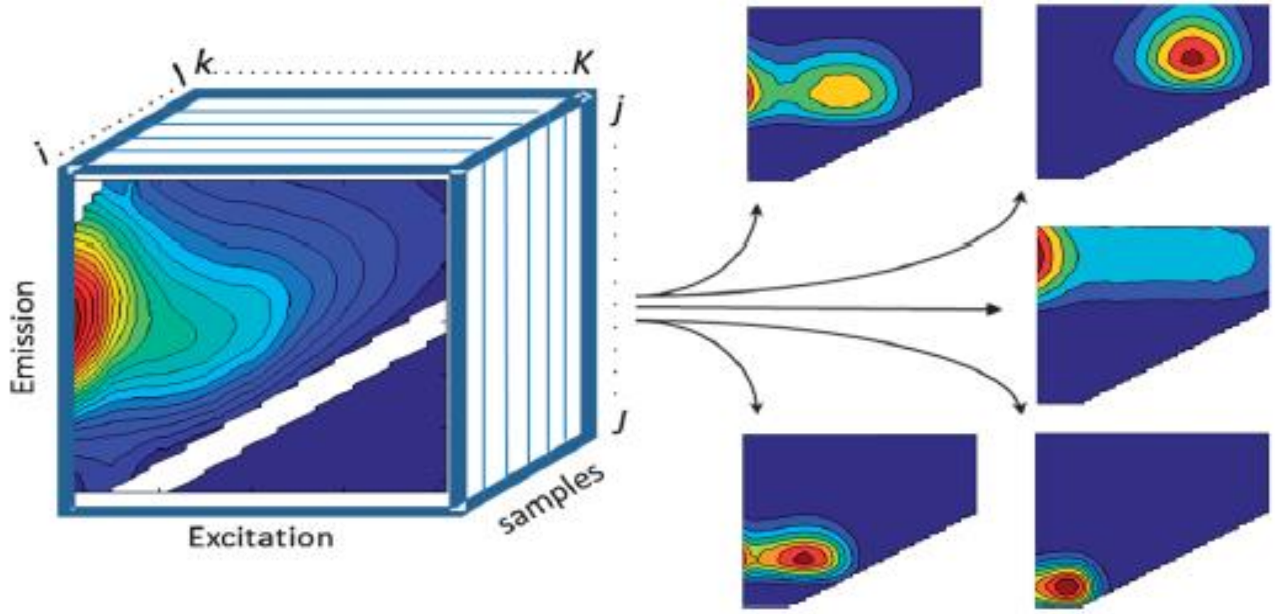


Fig. 2 EEM dataset arranged in a threeway structure and decomposed into five PARAFAC components.

$$x_{ijk} = \sum_{f=1}^{F} a_{if} * b_{jf} * c_{kf} + e_{ijk}$$

Anal. Methods, 2013, **5**, 6557–6566

- Spectral analysis (UV-VIS spectrum) of solutions with unknown composition, like soil extractions
- The obtained spectrum is composed from different groups of OM molecules
- Chemometrics are applied for identifying spectral components, which can be related to more specific chemical groups / materials. The obtained components are also quantified by scores, expressing their relative concentration in the measured sample.

Soil health project – Israel – Experimental design

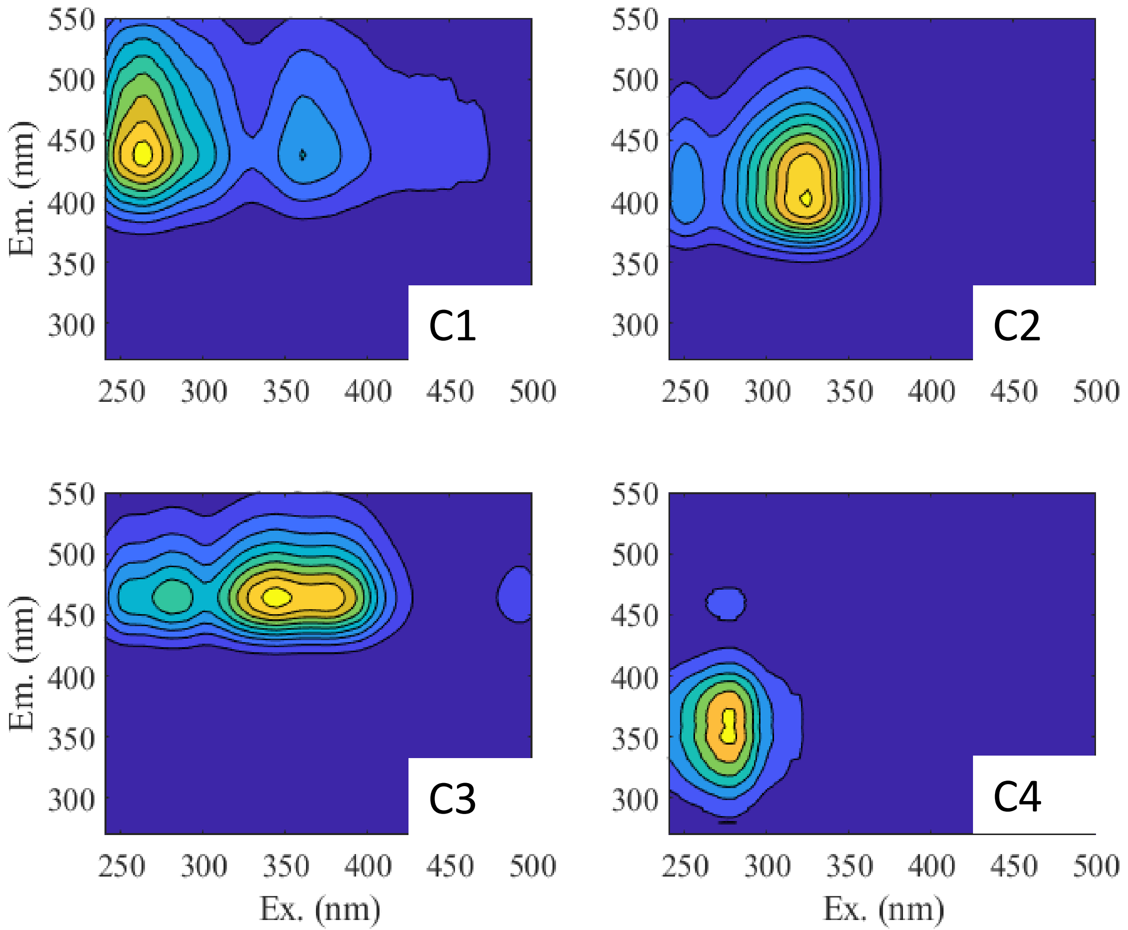
- 2 main agricultural regions – northern valleys and western Negev
- 3 sampling sites in each region
- 3 different land uses in each site - field crops, orchards and uncultivated adjacent plots
- 3 replicates (pits)
- 4 sampling depths

Overall = 216 samples (one sampling season)

Water extractions (1:2 soil : water ratio): DOC, EEM

PARAFAC components – soil health project

#	Ex.	Em.	Description	Reference
C1	265 (360)	438	Terrestrial (plant derived), related to microbial modification of organic matter	(Jørgensen et al., 2011; Yamashita et al., 2010)
C2	(250) 325	402	Humic-like, common in wastewater and agricultural catchments	Borisover et al. 2012, Lambert et al. 2017
C3	(280) 345-375	464	Terrestrial humic-like, widespread in freshwaters, associated with aromatic molecules of high molecular weight	Lambert et al., 2017
C4	275	352-364	Tryptophan-like, aliphatic, low MW	Lambert et al., 2016, Fellman et al. 2010, Rinot et al. 2018.



Sampling region and land use effects on DOC and Fmax values (±standard error) of the obtained PARAFAC components of EEM data for soil water extractions – soil health project, upper soil layer (0-10cm)

Land use	DOC (mg/l)	F1	F2	F3	F4
Field crops	38.51 (5.51)	1.68 (0.25)	1.66 (0.31)	4.25 (0.86)	5.96 (1.13)
Orchards	33.57 (5.05)	1.37 (0.25)	2.75 (0.35)	6.48 (0.91)	5.57 (0.93)
Uncultivated	37.14 (4.69)	1.40 (0.21)	1.04 (0.13)	2.78 (0.31)	4.57 (0.53)

Analysis of variance (ANOVA) – Upper soil (0-10cm)

Parameter	Land use	Region	Plot*Region
TDN (mg/l)	0.03	--	--
DOC (mg/l)	--	--	--
ABS_{254nm}	--	0.05	0.01
SUVA	--	0.014	0.02
F1	--	--	--
F2	0.047	0.007	0.001
F3	0.036	0.013	0.0004
F4	0.039	--	--
F1/DOC	--	0.034	--
F2/DOC	0.0007	0.0001	0.002
F3/DOC	0.0012	0.0005	0.002
F4/DOC	--	--	--

p-values of ANOVA tests, representing significant ($p<0.05$) effects of land use and sampling region on the measured and calculated values of soil water extracts.

Non-significant values ($p>0.05$) are not presented.

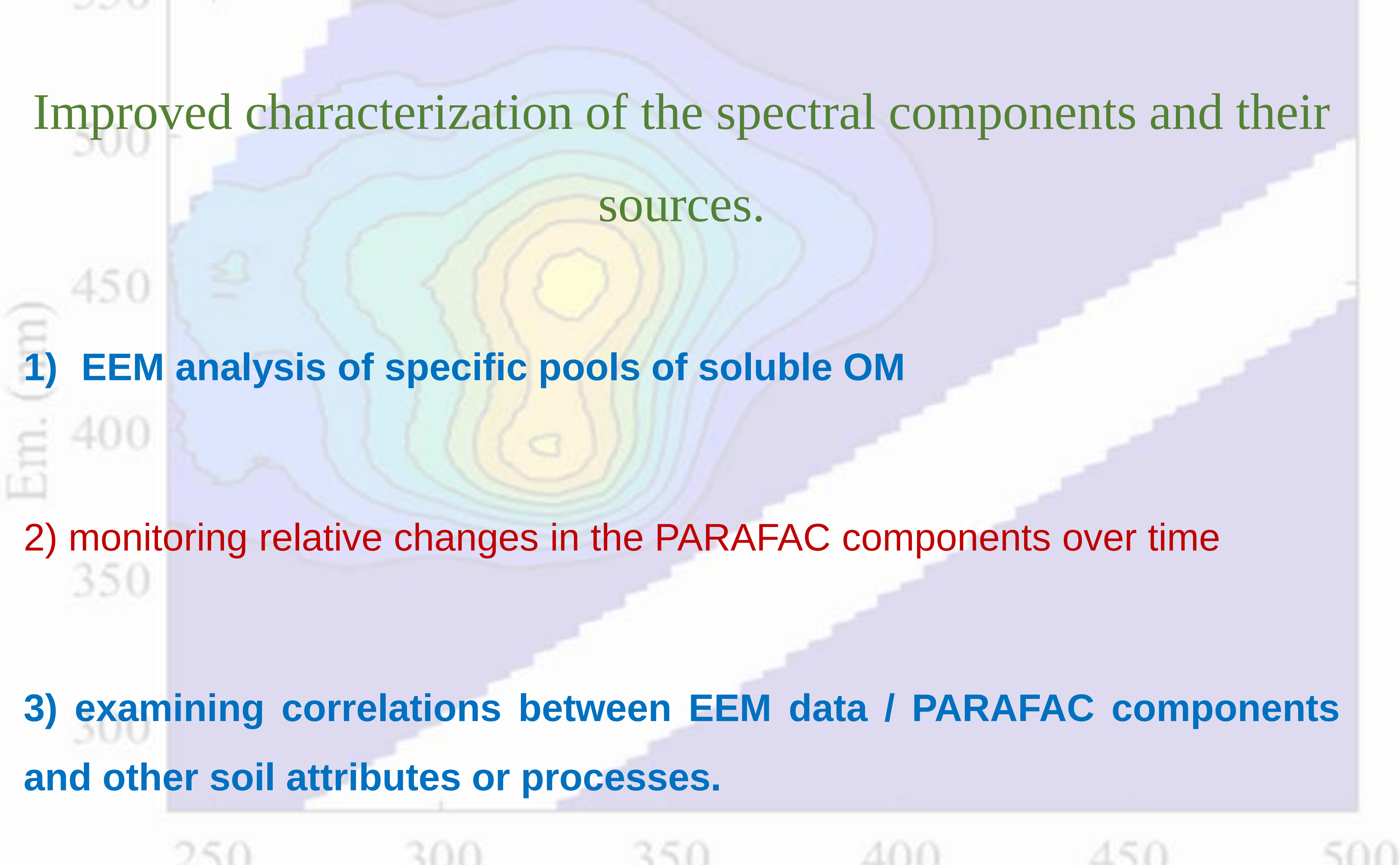
Demonstration of the sensitivity of the EEM-PARAFAC components to detect changes in WEOM between different land uses which may confirm their potential as soil health indicators.

Improved characterization of the spectral components and their sources.

1) **EEM analysis of specific pools of soluble OM**

2) monitoring relative changes in the PARAFAC components over time

3) **examining correlations between EEM data / PARAFAC components and other soil attributes or processes.**

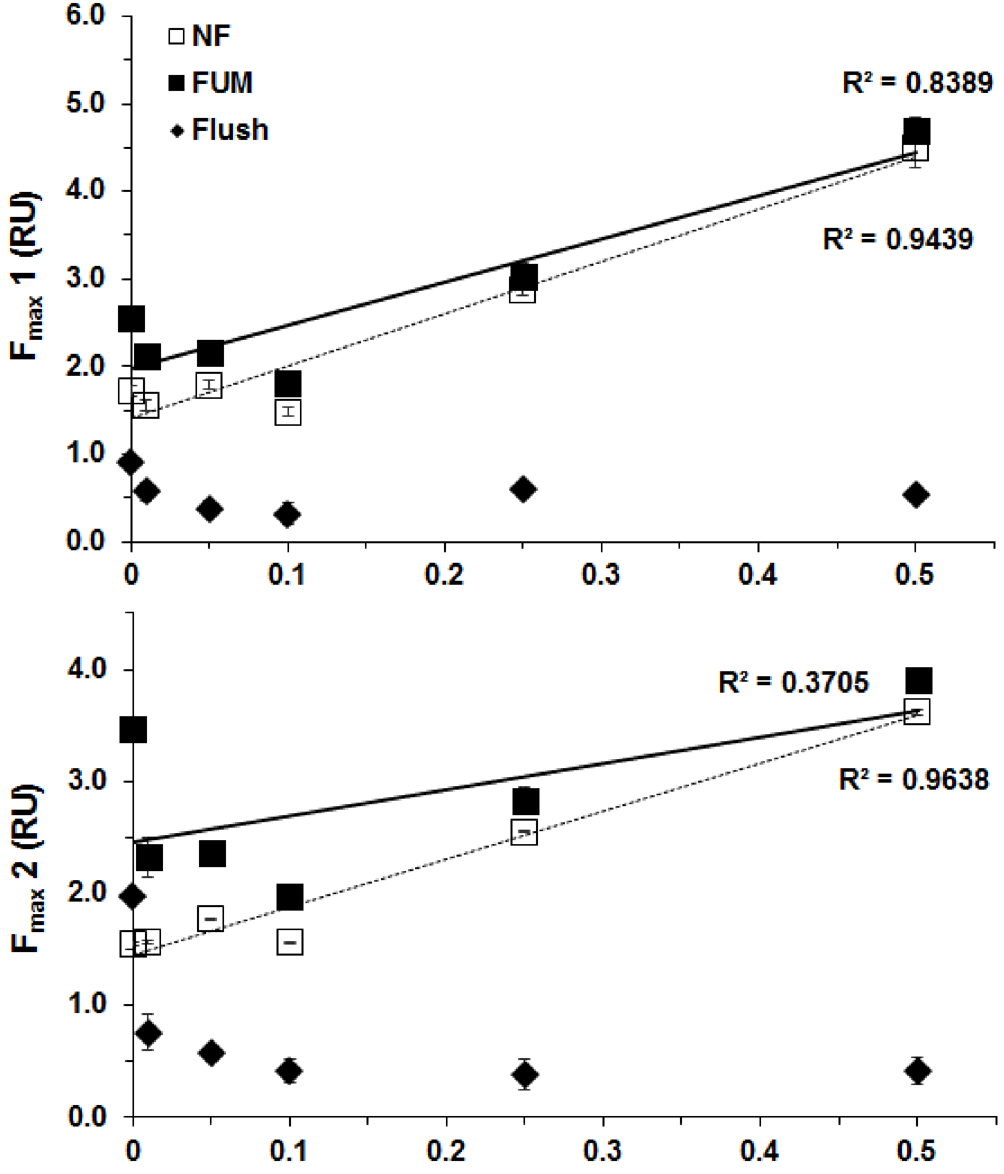


New insights from fluorescence spectroscopy into the composition of chloroform fumigation-extractable soil organic matter

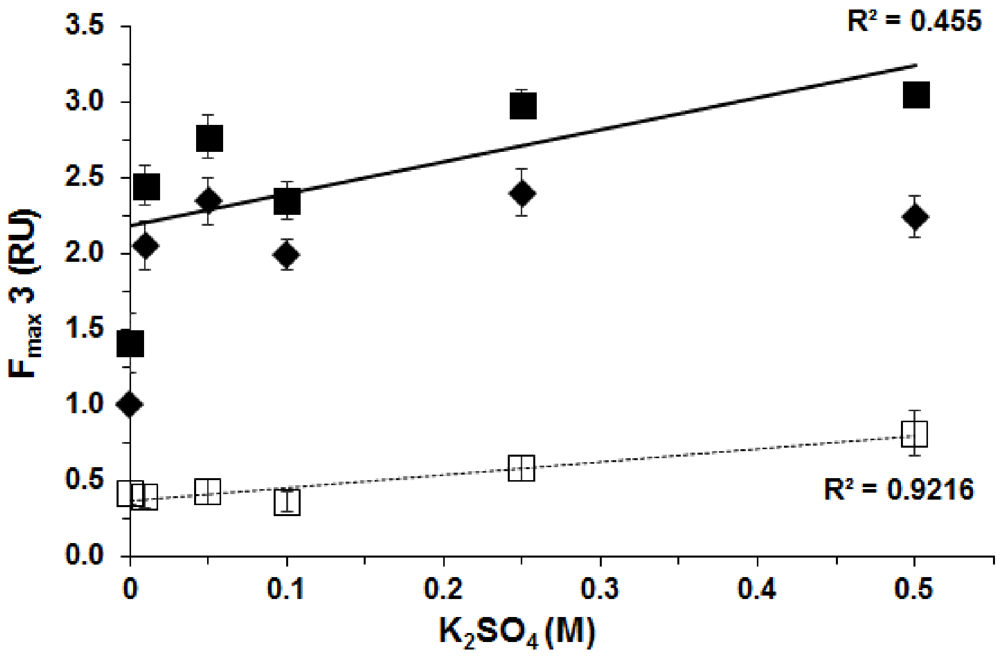
- Fluorescence spectroscopy coupled with PARAFAC was employed for the characterization of chloroform fumigation-extractable soil organic matter commonly used to estimate microbial biomass.

- A non-rhizosphere Vertisol was assayed under increasing K_2SO_4 extractant molarity (0-0.5 M) which allowed increasing organic matter extractability levels and the association of these increases with relative contributions from microbial versus humic sources.

Humic-like components



Tryptophan-like component



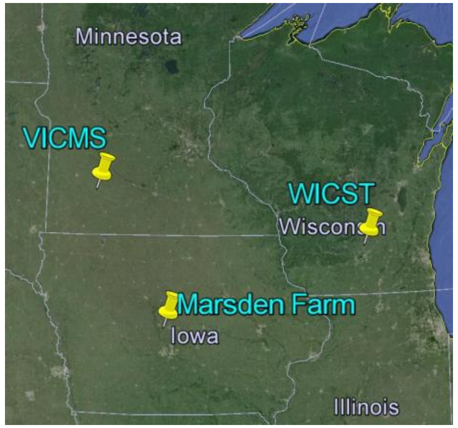
Discriminating between contributions from humic (i.e., non-cellular) and microbial tryptophan-like, fumigation-extractable soil organic matter

EEM fluorescence spectroscopy of soil water extractable organic matter to predict gross and potential N mineralization rates in various soils.

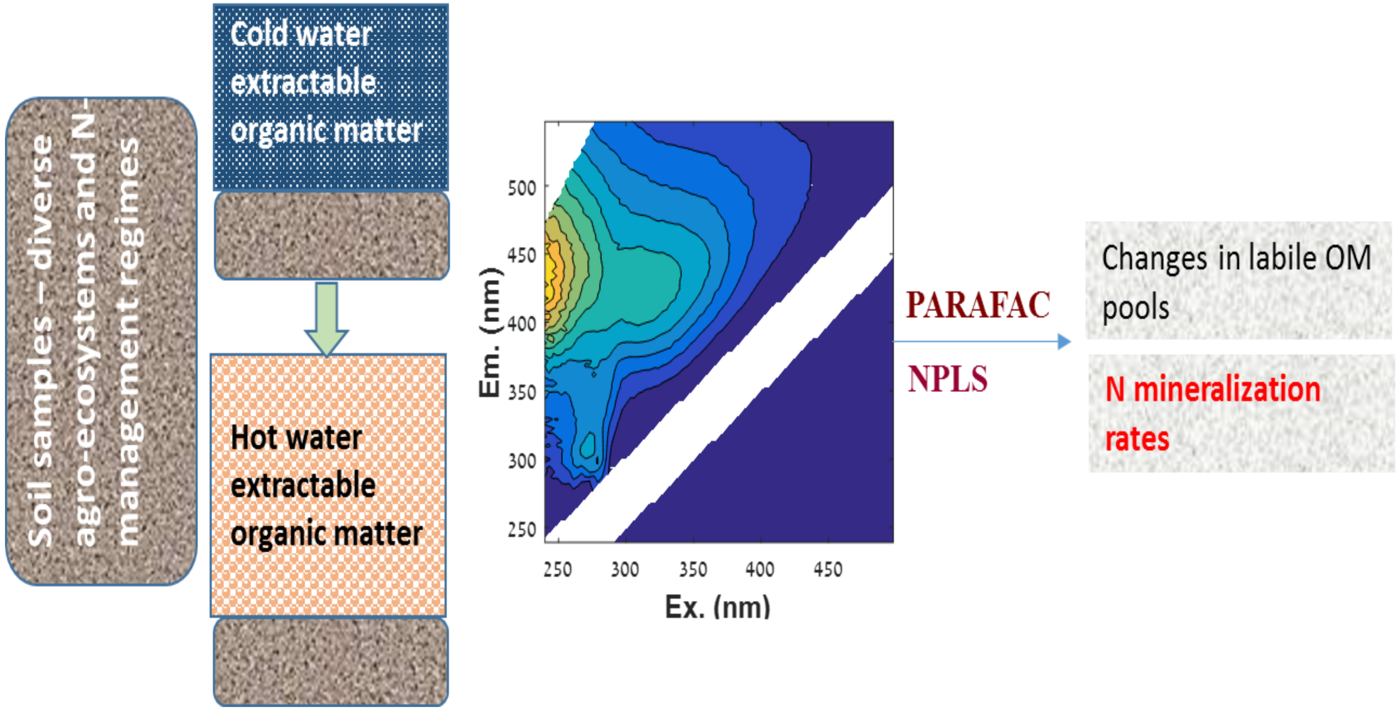
Hypotheses

- EEM spectroscopy along with PARAFAC analysis of soil water extracts may provide better detection of changes between characteristic organic components of various soils, and effects of environmental and agronomic practices (e.g. fertilizations, crop rotations, organic amendments) on the soils.
- PARAFAC components may serve as predictors for N mineralization and other parameters when applying single or multiple linear correlations for specific sites and/or in various agricultural environments.
- NPLS modeling of EEM data of soil water extracts may provide effective, potentially universal and "easy to get" prediction of gross and potential mineralization rates and also other parameters such as TOC, TN.

Methods

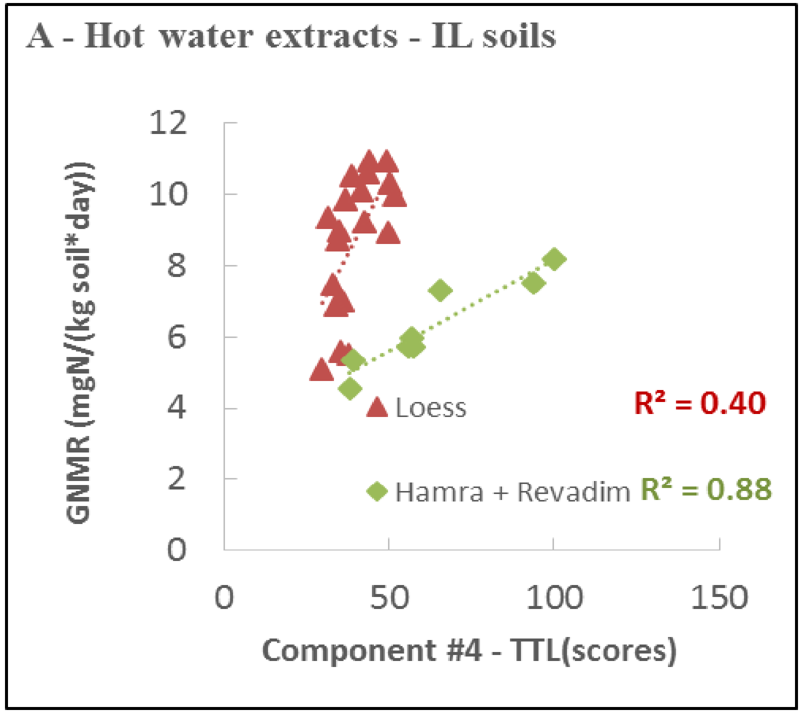


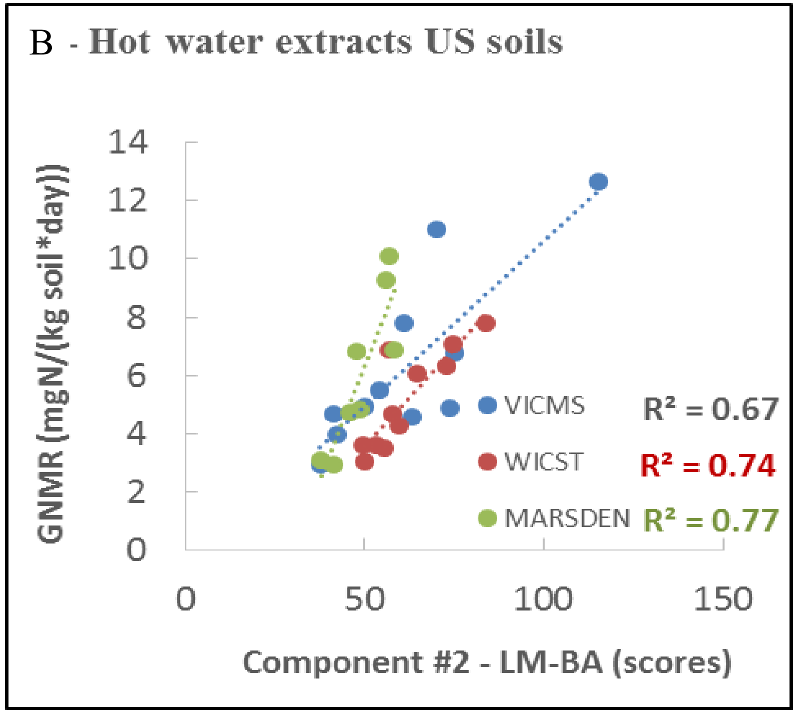
- Treatments in each experiment consisted of different cropping systems as well as N fertility managements.
- Measured **gross N mineralization** by ^{15}N pool dilution, and **potential net N mineralization** by anaerobic 7-day incubation (PMN).
- Cold and hot water extractions + EEM fluorescence spectroscopy analysis.
- PARAFAC and NPLS modeling.



Oshri Rinot, William R. Osterholz, Michael J. Castellano, Raphael Linker, Matt Liebman and Avi Shaviv (2018) Excitation-Emission Matrix fluorescence spectroscopy of soil water extracts to predict nitrogen mineralization rates. SSSAJ, 82:126-135.

Gross N mineralization prediction by PARAFAC components – Hot water

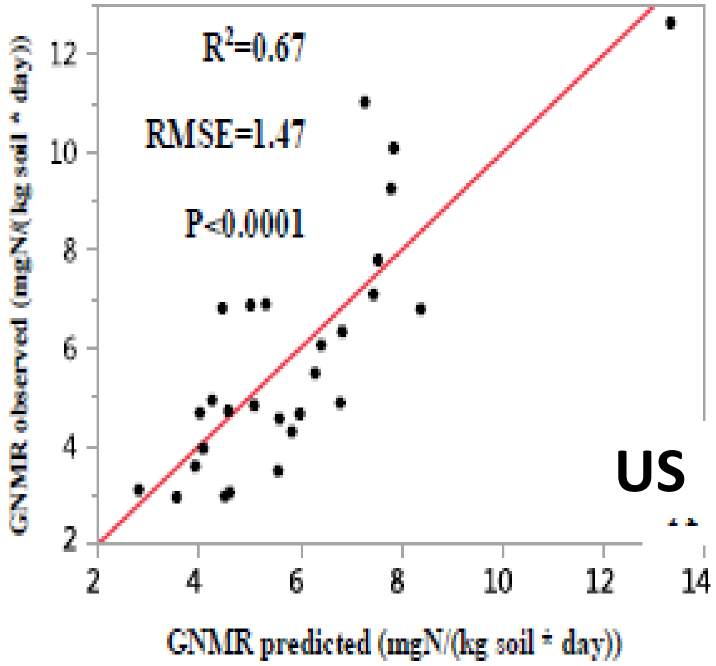


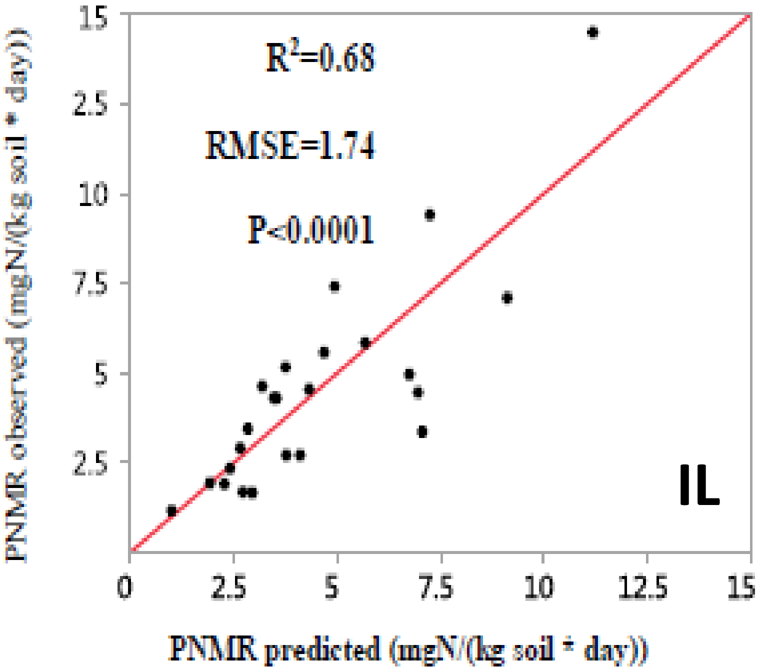


"Site-specific" or "overall" correlations?

Potential N mineralization prediction by PARAFAC components – Hot water

Multi-linear regressions – PLS model





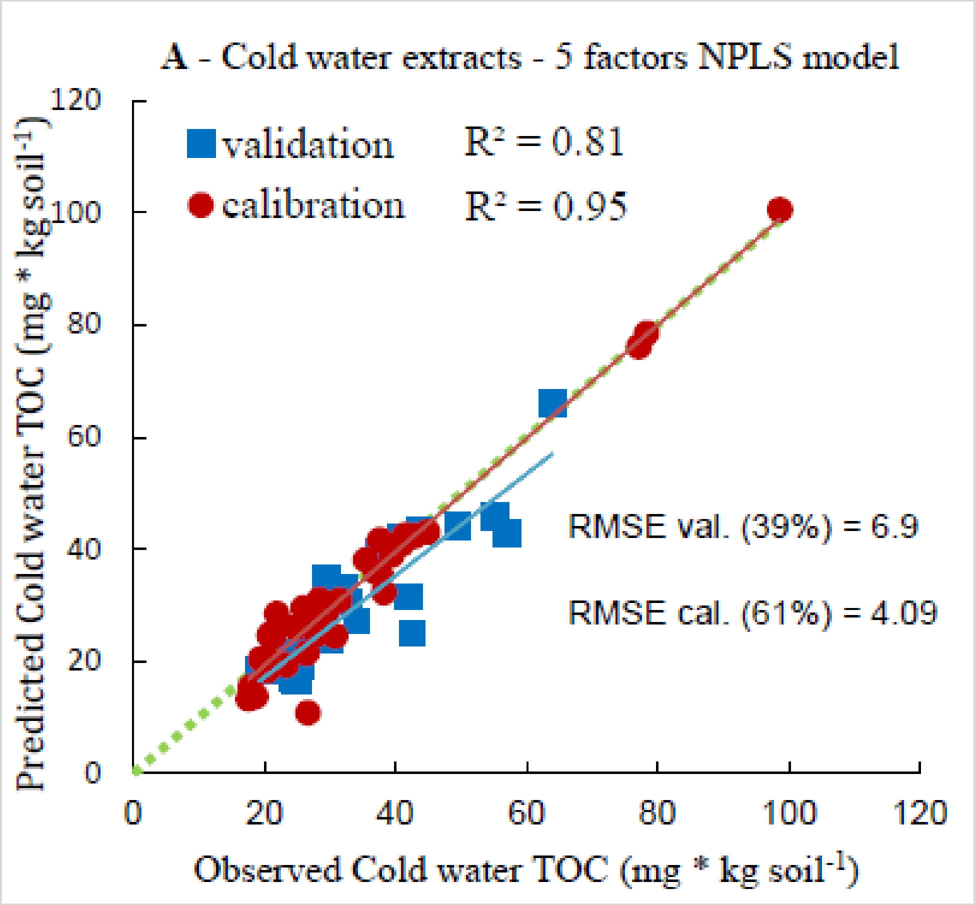
GNMR (US soils) = 0.14***comp3** (TL) + 0.12***comp4** (HM-FA)-1.21

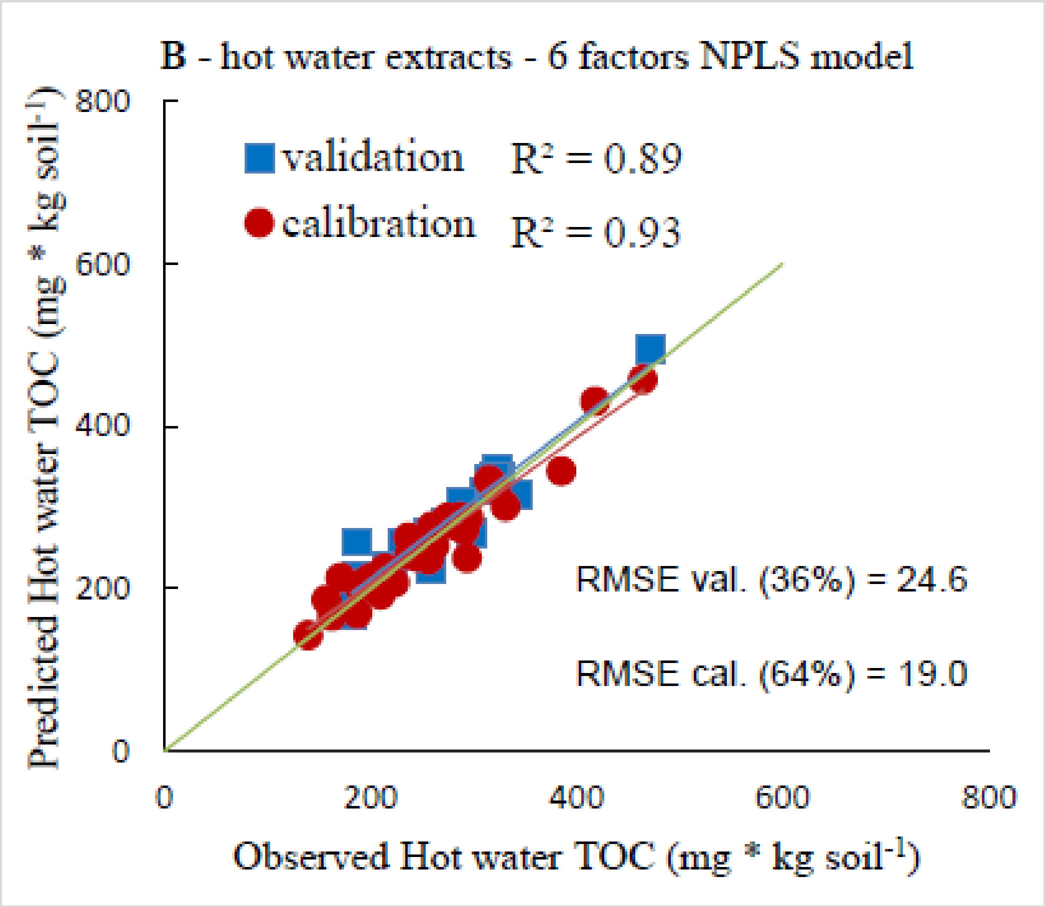
PNMR (IL soils) = 0.13***comp3** (HM-FA) + 0.79***comp4** (TTL)-24.29

NPLS modeling – Cold and Hot Water Extractable TOC – IL & US Soils

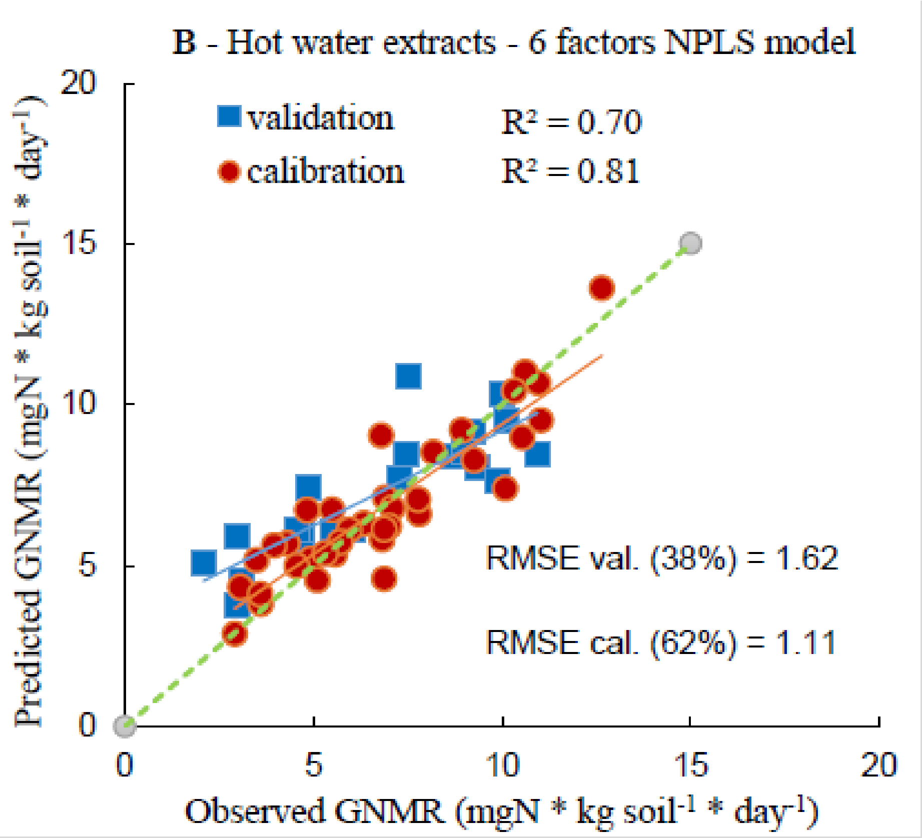
$$x_{ijk} = t_i w_j^{\,J} w_k^{\,K}$$

$$\max[\mathrm{cov}(t, y) \mid \min(\sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{k=1}^{K}(x_{ijk} - t_i w_j^{\,J} w_k^{\,K})^2)]$$

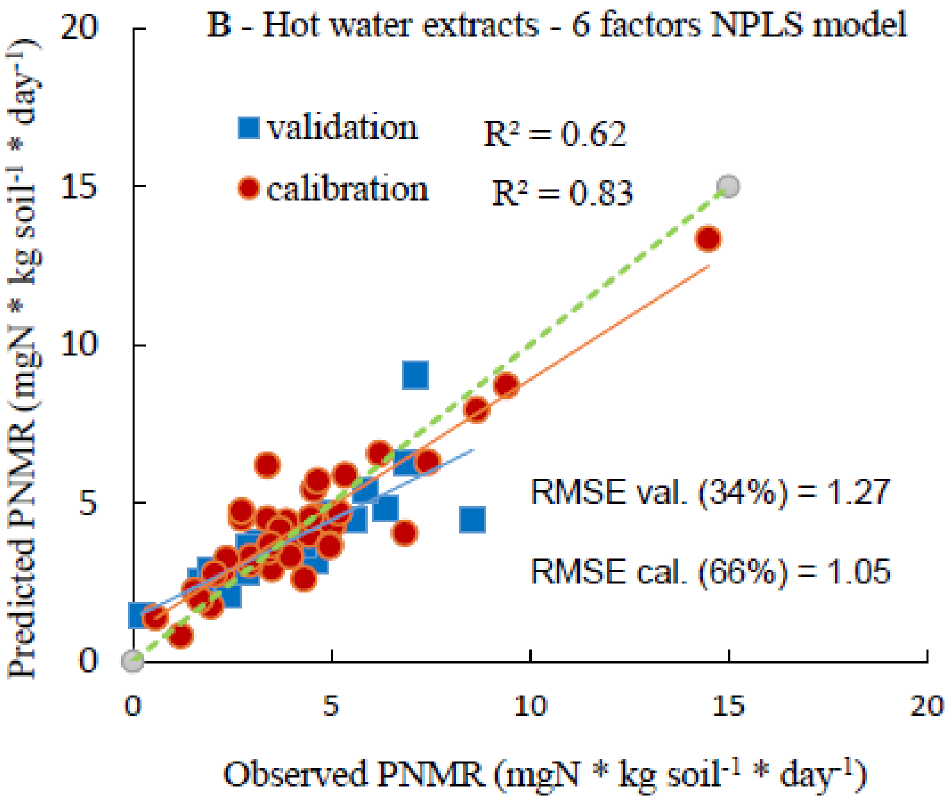




NPLS modeling – Gross and potential N mineralization rates – IL & US Soils



Gross N mineralization rate



Potential N mineralization rate

Conclusions

- **EEM-PARAFAC components can serve as sensitive indicators for characterization of DOM.**
- **EEM spectroscopy discriminated humic from proteinaceous fumigation-extractable SOM**
- **Changes in PARAFAC components over time assist in monitoring soil N dynamics.**
- **EEM data can provide reasonable prediction of relevant soil attributes and processes**


Thanks!
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