FTIR spectral properties affected by OM-cation interactions

R. H. Ellerbrock, H. H. Gerke[1]

[1]Leibniz Centre for Agricultural Landscape Research (ZALF) e.V., Programm Area Landscape Processes, WG Hydropedologie, Müncheberg;

Leibniz-Zentrum für Agrarlandschaftsforschung (ZALF) e.V.

Programm Area Landscape Processes

CC BY

Introduction and Objective

Soil organic matter (OM) interacts with cations like Ca by using C=O and OH functional groups. Such interactions are known to protect soil OM against decomposition. Interaction with cations may affect the bonding strength of the respective functional groups. Chnages in bonding strength are known to shift the wavenumber region of OH and C=O absorption band maxima in Fourier transform infrared (FTIR) spectra. The aim is to analyze the extent of such shifts to determine presence and strength of OM–cation interaction.

Material and Methods

Mucilage collected from Chia seeds (Muci; Ahmed et al., 2014), Polygalacturonic acid (PGA; Roth) and humic acid (HS; Aldrich) were mixed with CaCl2 solution at different OM : cation ratios (Table 1). For each OM components water based storage solutions were prepared as follows: The OM was mixed with 1000 ml of water and treated for 30 minutes in an ultrasound bath to ensure a dispersion as complete as possible. Than an aliquot of 50ml was taken and further diluted to 5000 ml to resulting in 0.01 mmol OM solutions. Aliquots of them (PGA, Muci, HS) were than mixed with 0.01 M CaCl2 solutions in water. Each mixture was stirred for 2 hours, freeze dried and analyzed using FTIR spectroscopy in KBr-technique. The ratios between the intensities of C-H and C=O bands (C-H/C=O), of C=O and C-O-C bands (C=O/C-O-C) and between $C=O_{cat}$ and C-O-C band (C=Ocat/C-O-C) were determined from the FTIR spectra.

Table 1 Mixing ratios of OM components (PGA, MUCI, HS) with 0.01 M $CaCl_2$ in water .

	OM:Ca[2]	PGA	Mucilage	Humic acid	CaCl2
Mixture	Ratios	1ml about 0.01 mmol of C=O groups			1ml=0,01mmol
1	3:1	30	30	30	10
2	3:1	30	30	30	10
3	6:1	60	60	60	10
4	6:1	60	60	60	10
5	9:1	45	45	45	5
6	9:1	45	45	45	5
7	12:1	60	60	60	5
8	12:1	60	60	60	5

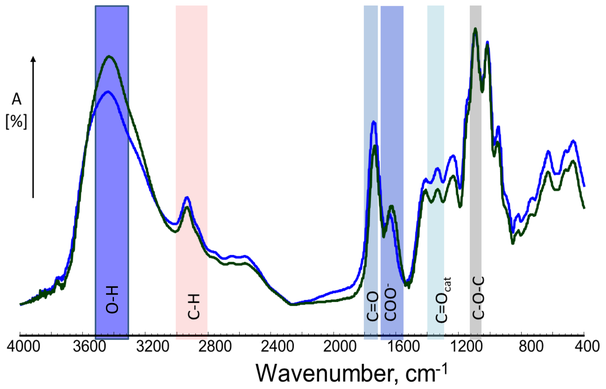

Fig. 1 FTIR spectra of PGA samples with colums indicating the regions of C-H; C=O, COO^-, $C=O_{cat}$ and C-O-C bands used to characterize the OM components (e.g. Capriel et al.,1995, Ellerbrock et al. 2005, Alvarez Puebla, 2005).

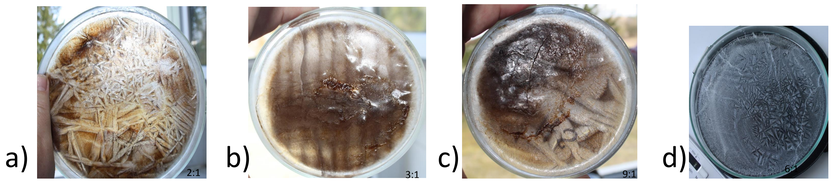

Fig. 2 Fotos of freeze dried mixtures of 0.01 M Humic acid with 0.01 M $CaCl_2$solutions at a) 3:1, b) 5:1 and c) 2:1 ratios and d) of mucilage mixed with CaCl2 at 6:1 ratio.

Summary & Conclusions

Addition of $CaCL_2$ affected the spectral data of all OM components.

Band shift in OM-CaCl2mixtures relative to intial OM

- strongest for COO^- and $C=O_{cat}$ bands in FTIR spectra of **PGA** (Fig. 5b).
- OM:Ca ratio of 0.33 ➔ only shift of C=O band for **HS** (Fig. 3a).
- For **mucilage** shift of O-H band most pronounced (Fig. 3c).

C-H/C=O ratios in OM-$CaCl_2$mixtures relative to initial OM

- C=O/C-O-C decreased with increasing PGA:Ca ratio for PGA & HS
- This is vice versa for C-H/C=O.
- Mucilage mixtures show much smaller changes, possibly caused by relative short equilibration time.
- In general CH/C=O decreased with increasing C=O/C-O-C (Fig. 4).

➔OM-Ca^{2+} interaction caused changes in FTIR spectra relative to initial OM indicating changes in OM properties.

➔ Extent of such changes (i.e., band shift and CH/C=O ratios) relative to initial OM depend on the kind of OM.

➔When interpreting the FTIR spectra with respect to OM content and composition above mentioned effects need to be considered.

Results and Discussion

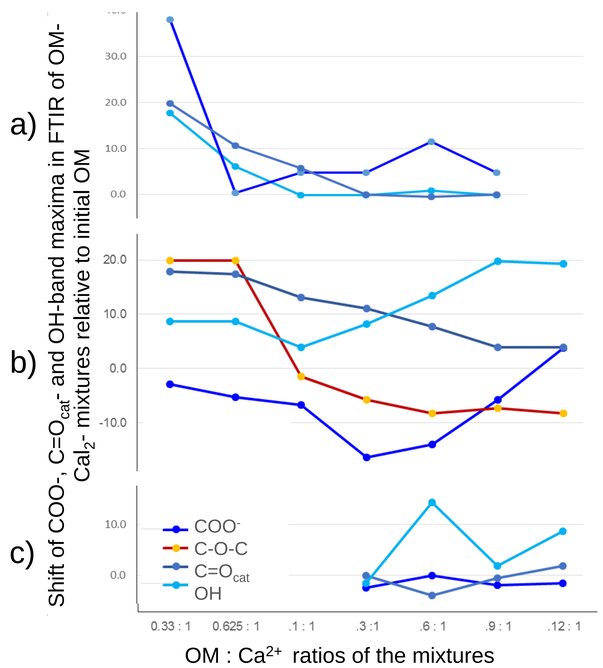

Fig. 3 Shift in the WN of COO-, $C=O_{cat}$-, C-O-C- and OH- band maxima in FTIR spectra of OM-$CaCl_2$ mixtures relative to the ones in FTIR spectra of the initial OM (: a) PGA, b) Muci, c) HS).

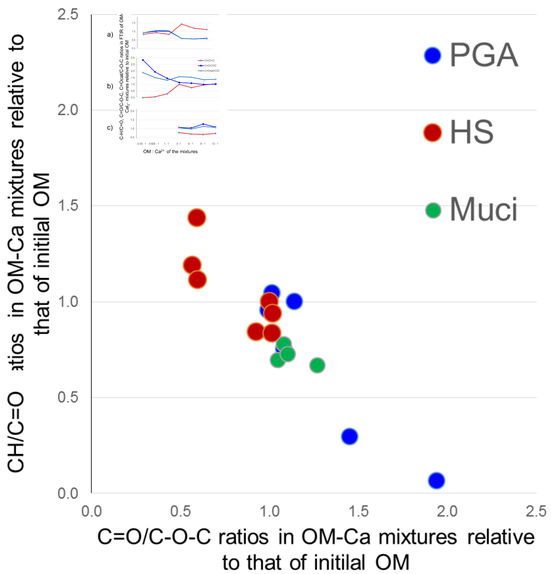

Fig. 4 C-H/C=O ratios vs C=O/C-O-C ratios (of OM-$CaCl_2$ mixtures relative to those of initial OM). Insert shows the respective ratios per each mixture for a) PGA, b) Muci & c) HS.

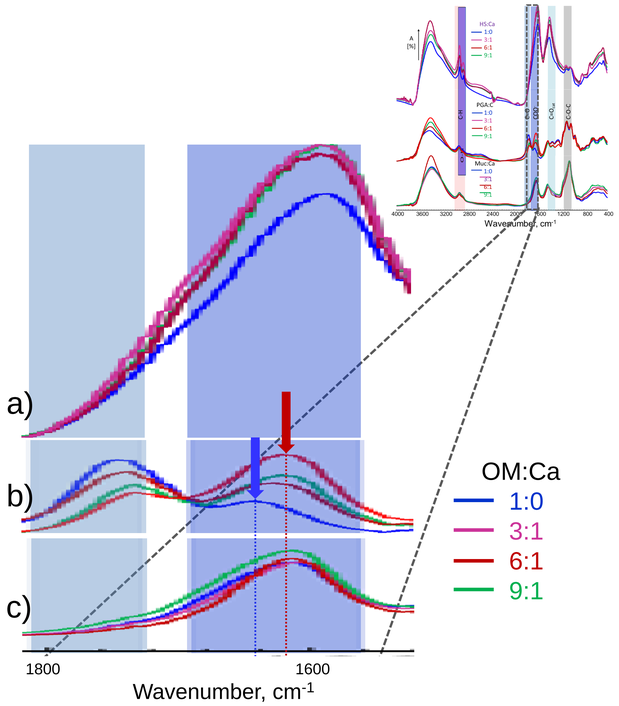

Fig. 5 COO^- bands (WN 1575 to WN 1850 cm-1) in FTIR spectra of OM-$CaCl_2$ mixtures (a) Humic acid, b) PGA and c) mucilage). (Insert: FTIR spectra from 400 to 4000 cm-1 normalized to C-O-C band.)

References

Ahmed, M. A., et al. 2015: Effect of soil drying on mucilage exudation and its water repellency: a new method to collect mucilage. J. Plant Nutr. Soil Sci. 178, 821-824.

Capriel, P., et al. 1995. Hydrophobicity of the organic matter in arable soils. Soil Biol. Biochem. 27:1453–1458.

Ellerbrock R.H., et al. 2005. Composition of Organic Matter Fractions for Explaining Wettability of Three Forest Soils. Soil Sci. Soc. Am. J. 69:57–66 (2005).

Ellerbrock et al. 2019; Spectroscopic characterization of mucilage (Chia Seed) and polygalacturonic acid. J Plant Nutr. Soil Sci. 2019 in print; jpln.201800554.R3

rellerbrock@zalf.de

Acknowledgements

This study was financially supported by the German Federal Ministry of Food and Agriculture (BMEL) and the Ministry for Science, Research and Culture of the State of Brandenburg (MWFK).