Composition-Dependent Sorptive Fractionation of Anthropogenic Dissolved Organic Matter by Fe(III)-Montmorillonite

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Introduction

Natural organic matter is transported through soil profiles by water, where mineral-organic associations that form to retain dissolved organic matter (DOM) play a key role in terrestrial carbon cycling and beneficial features for agricultural applications and contaminant sequestration. Therefore, understanding the chemical composition of constituents capable of forming mineral-organic associations would provide insight into soil carbon sequestration and soil organic matter functions. This study implemented Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with novel data analysis techniques to examine the role of sorptive fractionation in associations between dissolved organic matter from composted biosolids (hereafter, "anthropogenic DOM") and Fe(III)-montmorillonite, a 2:1 clay with permanently charged surfaces. The following report includes excerpts from the published article.

Experimental

The bulk anthropogenic DOM was filtered and structurally fractionated into hydrophobic acidic (HoA), hydrophobic neutral (HoN), and hydrophilic neutral (HiN) fractions to be run alongside the bulk. DOM fractions were analyzed before and after batch equilibrium sorption experiments with Fe(III)-montmorillonite using negative ion mode electrospray ionization (ESI−) and the passively shielded 9.4 T FT-ICR MS at the Ion Cyclotron Resonance Facility of the National High Magnetic Field Laboratory (NHMFL). Custom software (PetroOrg©) was used for additional calibration and elemental composition assignment. Compositions between structural fractions were compared using R software and FactoMineR.

Results and Discussion

A large proportion (45 to 64%) of the initial carbon in every DOM solution sorbed to the Fe(III)-montmorillonite, with the highest percentage in the HoA fraction, attributed to higher carboxyl content. When the compositions of the initial solutions were compared to their sorbed organic matter extracts, the difference in composition was relatively low (10 to 32%). The degree of the sorptive fractionation seemed to be composition dependent, but the low difference between initial and sorbed compositions implies that non-selective sorption was more important than selective sorption in every sample, except for the HiN fraction, where high nitrogen content and acidic conditions appeared to enhance sorptive fractionation.

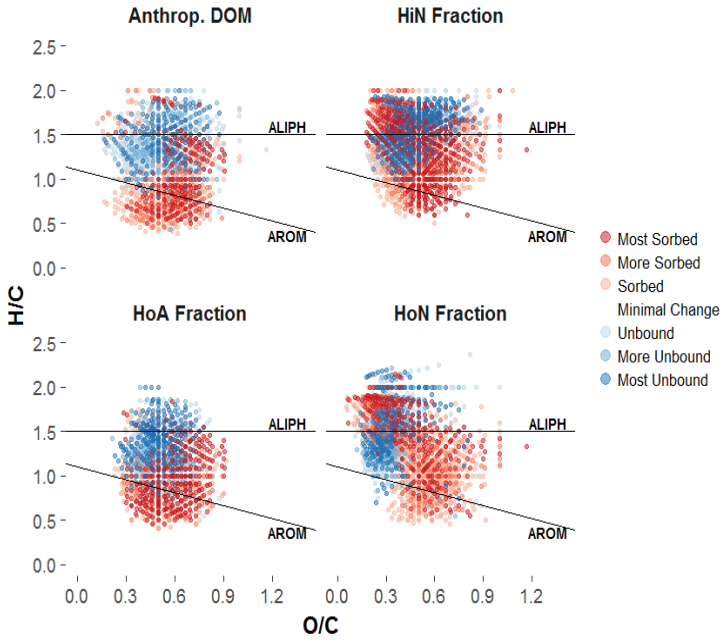

Fig.1 Van Krevelen Diagrams of common formulas between the initial and sorbed extracts of each DOM fraction, colored based on changes in relative abundance.

Conclusions

This study demonstrates that the importance of sorptive fractionation varies with DOM composition and other factors, and that non-selective sorption can contribute substantially to the formation of mineral-organic associations.

Acknowledgements

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References

[1] Young, R.B., *et al.*, Soil Systems, **2**(1), 14 (2018)