Use of mediated electrochemical analysis and high field FTICR mass spectrometry to explain humic acid fractionation upon sorption to redox inert sorbents

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Conformational arrangements might trigger changes in HA properties.

HALP: Humic Acid Like Polycondensate
A300: grafted HALP on SiO$_2$ particles

- A300 $\rightarrow$ 300% higher antioxidant activity than only HALP
Fractionation is caused by Humic Acid (HA) compositional heterogeneity

Galindo and Del Nero (2015)

- Enrichment of highly oxygen functionalized aromatic and aliphatic molecules on Al₂O₃ surface
Electrochemical Properties of Natural Organic Matter (NOM)

\[ \text{Electron Exchange Capacity (EEC)} = \text{Electron Accepting Capacity (EAC)} + \text{Electron Donating Capacity (EDC)} \]

\[ \text{EH} = -0.49 \text{V vs. SHE} \]

100% Reduced

\[ \text{hydroquinone} \]

NOM native sample

\[ \text{quinone} \]

\[ \text{EH} = +0.61 \text{V vs. SHE} \]

100% Oxidized

Accepted electrons

Donated electrons

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• Does sorption of HA onto redox inert surfaces trigger changes in HA chemical properties (in the absence of electron transfer)?... and to which extent?

• Which sorption phenomena (fractionation, conformational arrangements, etc.) lead to changes in HA properties?
• Anoxic conditions \((O_2 < 0.1\text{ppm})\)
• pH 7 (no buffer use – 0.1M KCl medium)
• Sorbents: Aluminium Oxide \((\text{Al}_2\text{O}_3)\), resin DAX-8
• Humic Acids: Elliott Soil (ESHA), Pahokee Peat (PPHA), Suwannee River (SRHA) – IHSS standards
Sorption level effect?

- **Al₂O₃**: ↑% sorbed HA → up to 300% higher EDC whole suspension
- **DAX-8**: ↑sorbed HA → ~ 50% lower EDC whole suspension
- Optical analysis (UV – EEM fluorescence) did not provide clear indication of HA fractionation

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Sorption mechanism? → $\text{Al}_2\text{O}_3$ vs. DAX-8?

- $\text{Al}_2\text{O}_3$: EDC suspension > EDC HA stock solution
- DAX-8: EDC suspension < EDC HA stock solution
- Above ~ 50% sorbed HA, EAC & EDC decreased in supernatants
Double Bound Equivalent (DBE)

FT-ICR mass spectrometry results

SRHA Stock Solution  Supernatant – DAX-8  Supernatant – Al₂O₃

Appearance of new compounds after sorption

- Al₂O₃ : significant difference at N°C > ~25 and DBE > ~15

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Existence Analysis

Polyphenolic compounds such as Tannin

non-sorbed compounds

Preferentially sorbed compounds

Additional processes taking place during sorption

PPHA (2649 formulas) SRHA (4137 formulas) ESHA (2065 formulas)

Common in PPHA

Common in SRHA

Common in ESHA

Unique in Stock

Unique in Stock

Unique in Stock

Unique in PPHA after

Unique in SRHA after

Unique in ESHA after

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• Fractionation of HA upon sorption was confirmed by mediated electrochemical and FT-ICRMS analysis.

• No significant selective sorption of HA at DAX-8.

• Strong selective fractionation of HA components occur upon sorption at Al₂O₃. Poly-phenolic (Tannin) like seem to be leading preferentially sorbed compounds.

• Investigate further processes occurring upon HA sorption at polar minerals.

• To study systems where the sorbent is redox active (clays and iron minerals).
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