



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

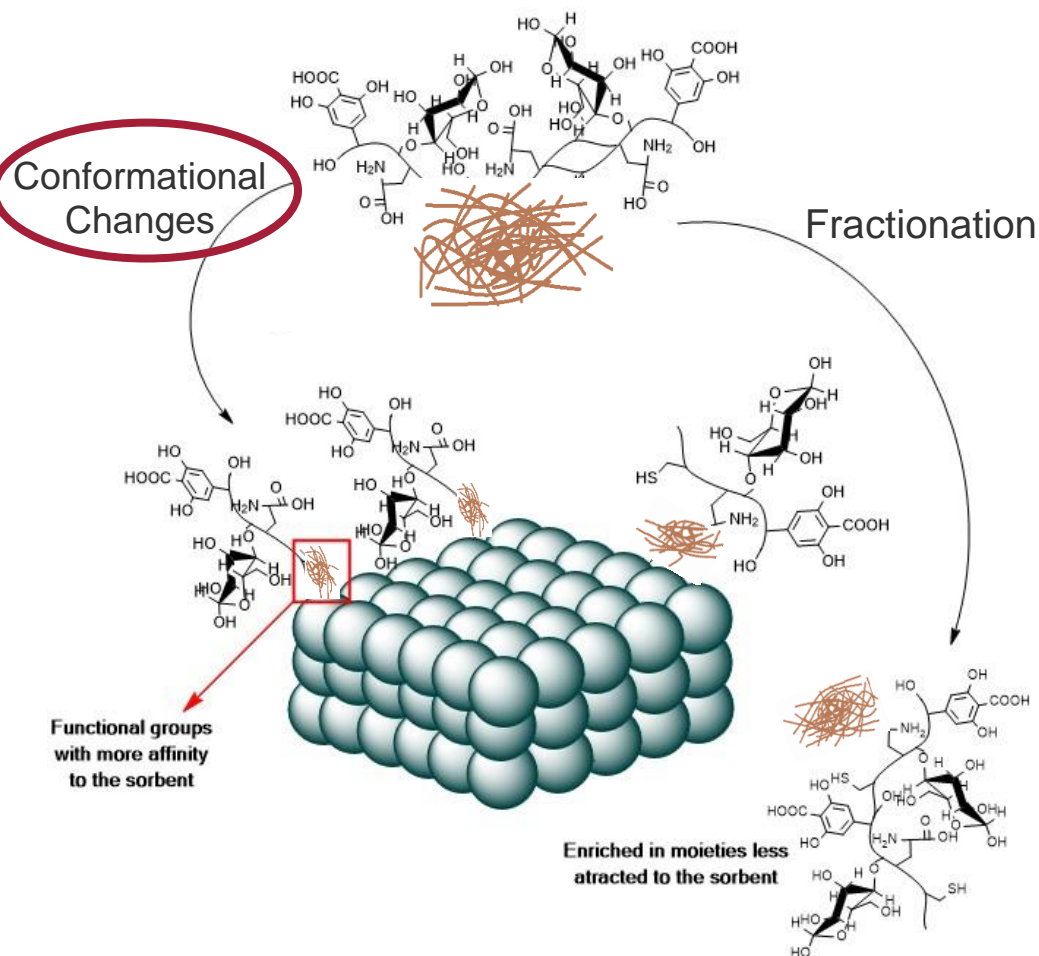
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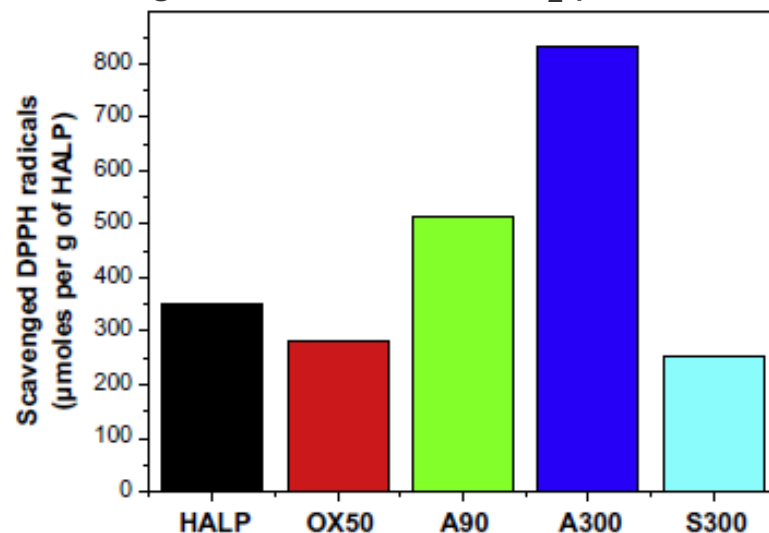
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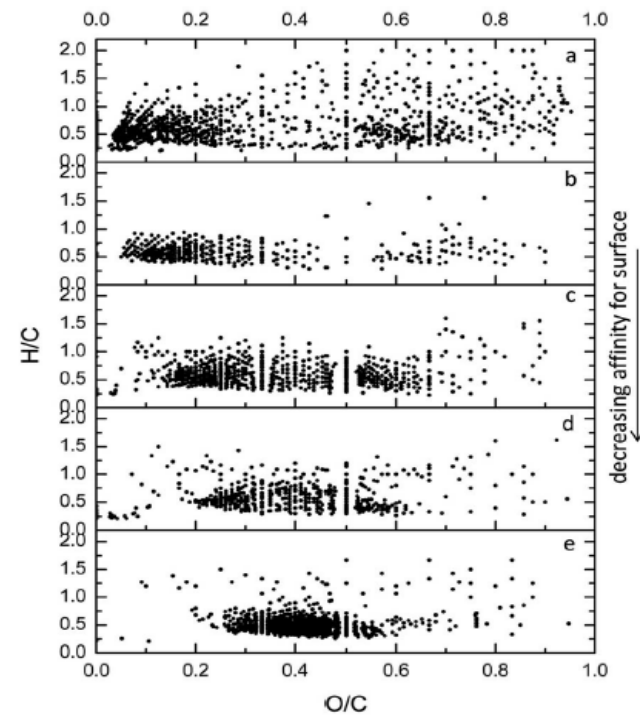
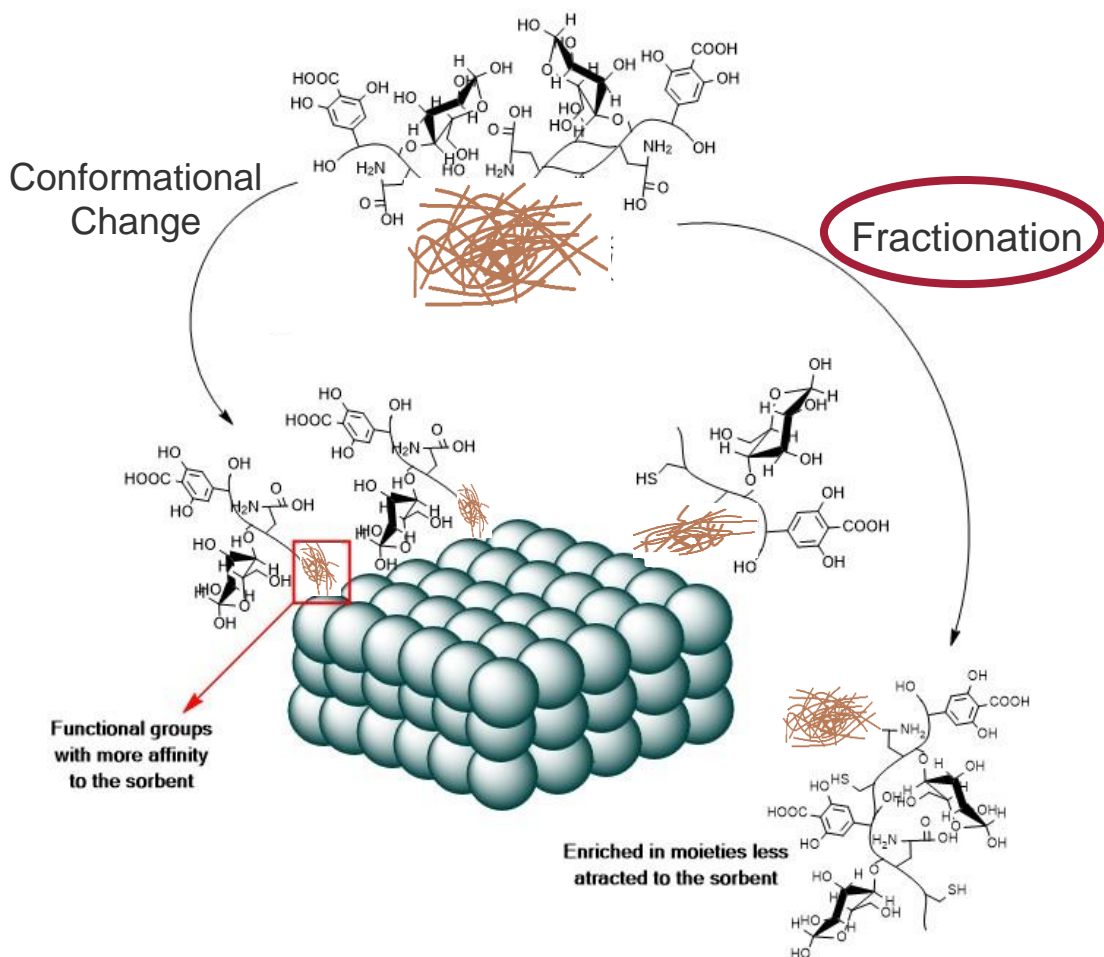
HALP: Humic Acid Like Polycondensate
A300: grafted HALP on SiO₂ particles



E. Bletsa et al. (2015)

- A300 → 300% higher antioxidant activity than only HALP

Conformational arrangements might trigger changes in HA properties.

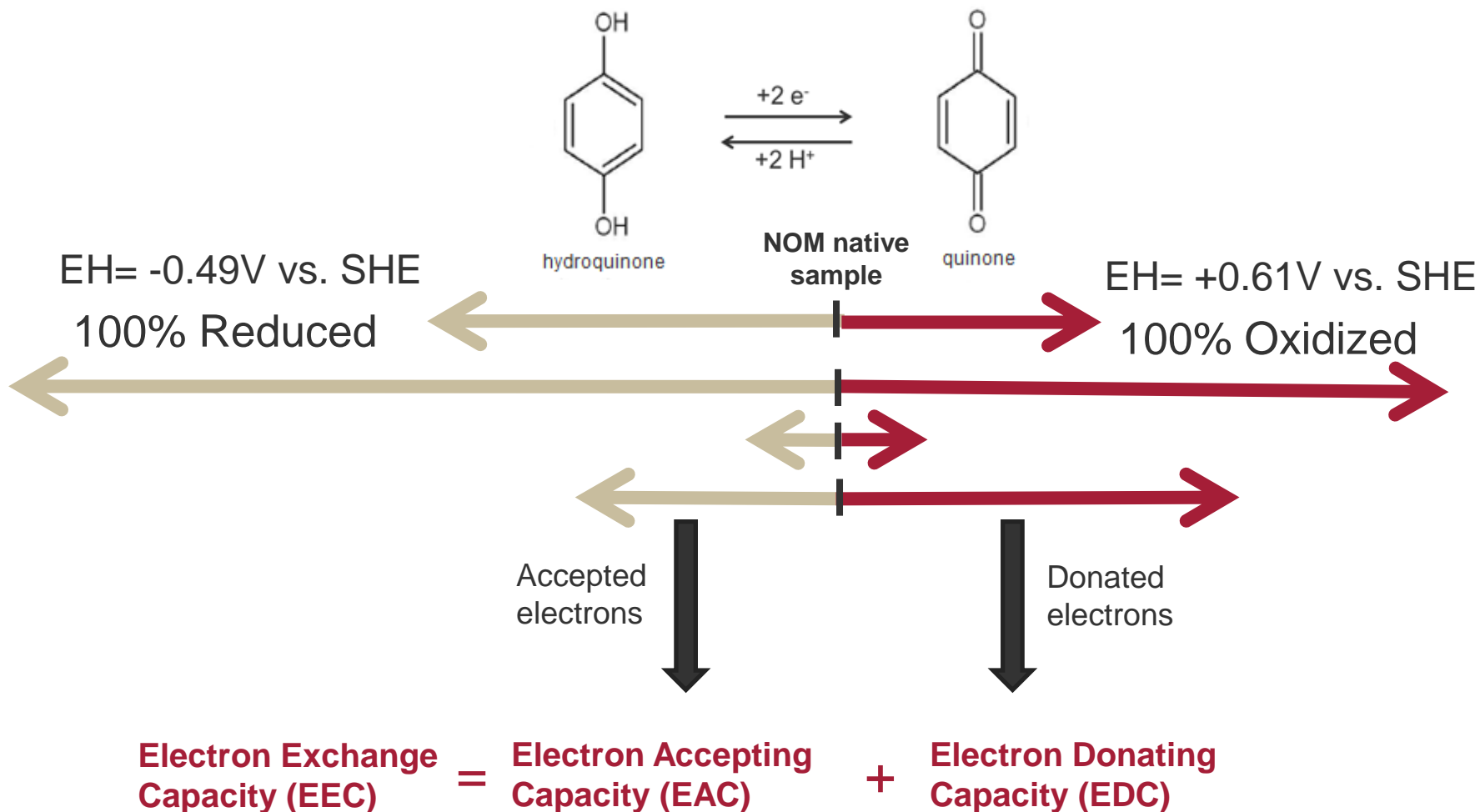


Galindo and Del Nero (2015)

- Enrichment of highly oxygen functionalized aromatic and aliphatic molecules on Al_2O_3 surface

Fractionation is caused by Humic Acid (HA) compositional heterogeneity

Electrochemical Properties of Natural Organic Matter (NOM)



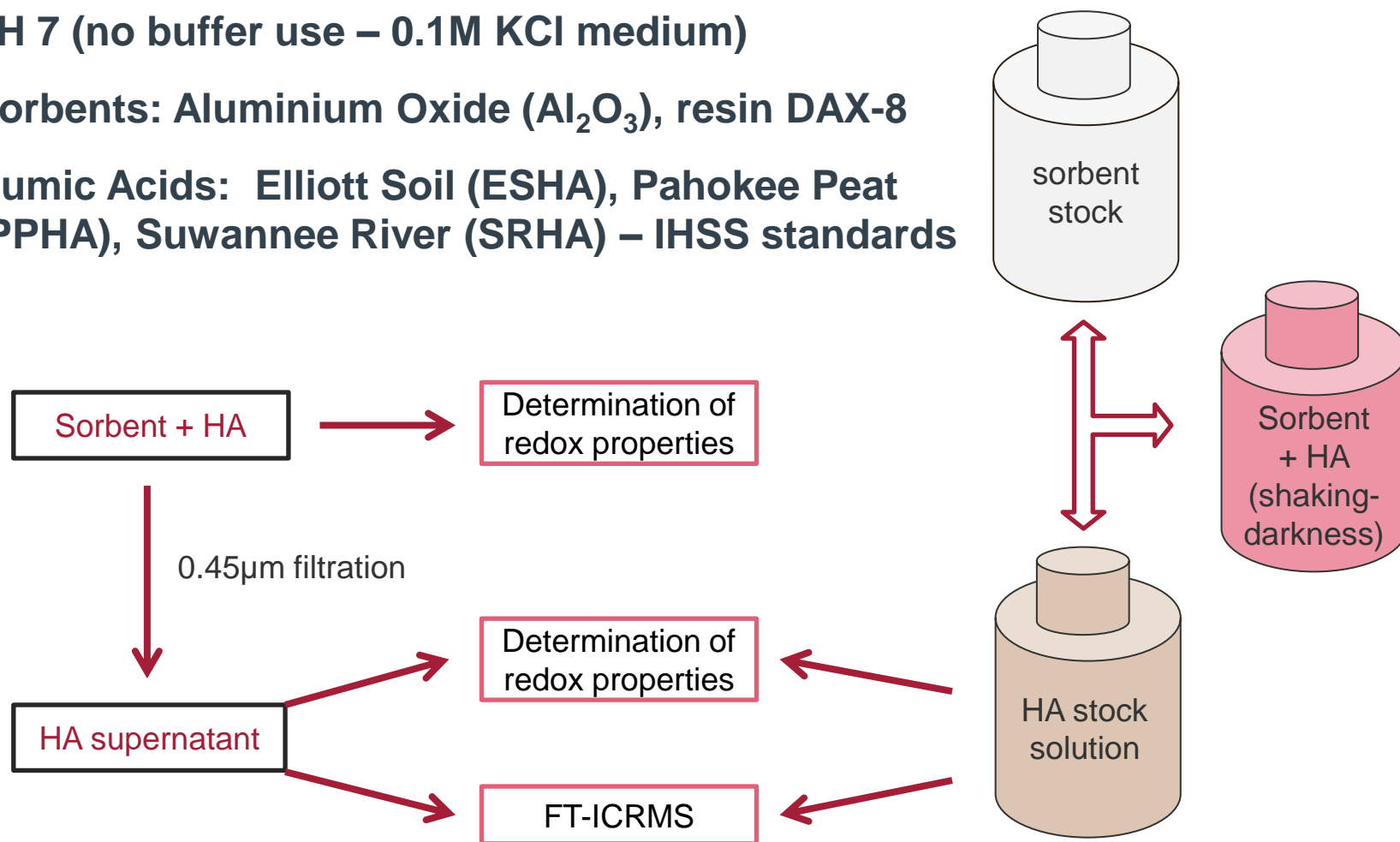


- **Does sorption of HA onto redox inert surfaces trigger changes in HA chemical properties (in the absence of electron transfer)?... and to which extent?**

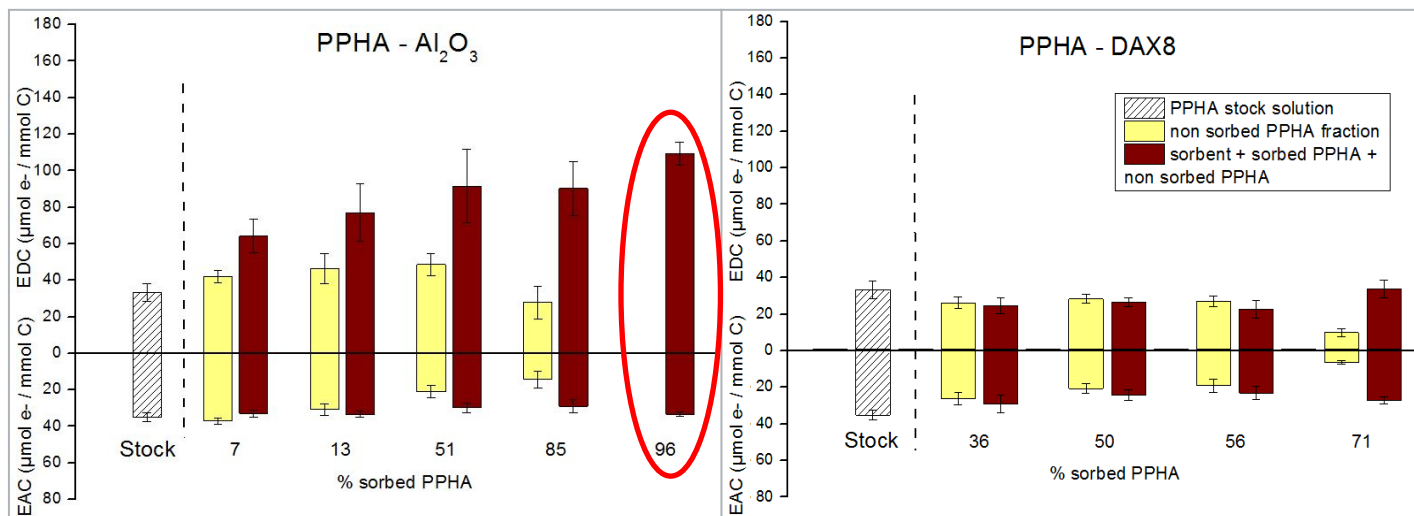


- **Which sorption phenomena (fractionation, conformational arrangements, etc.) lead to changes in HA properties?**

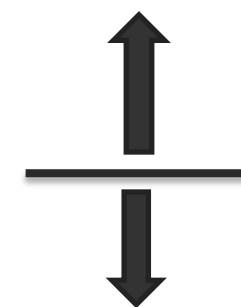
- Anoxic conditions ($O_2 < 0.1\text{ppm}$)
- pH 7 (no buffer use – 0.1M KCl medium)
- Sorbents: Aluminium Oxide (Al_2O_3), resin DAX-8
- Humic Acids: Elliott Soil (ESHA), Pahokee Peat (PPHA), Suwannee River (SRHA) – IHSS standards



Sorption level effect?



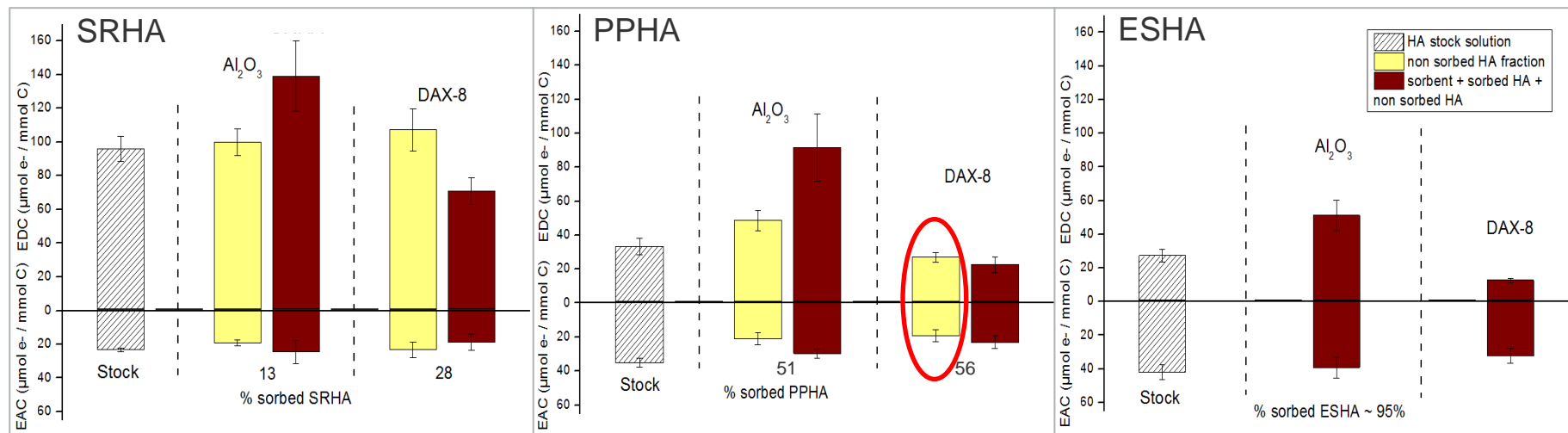
more reduced



more oxidized

- **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

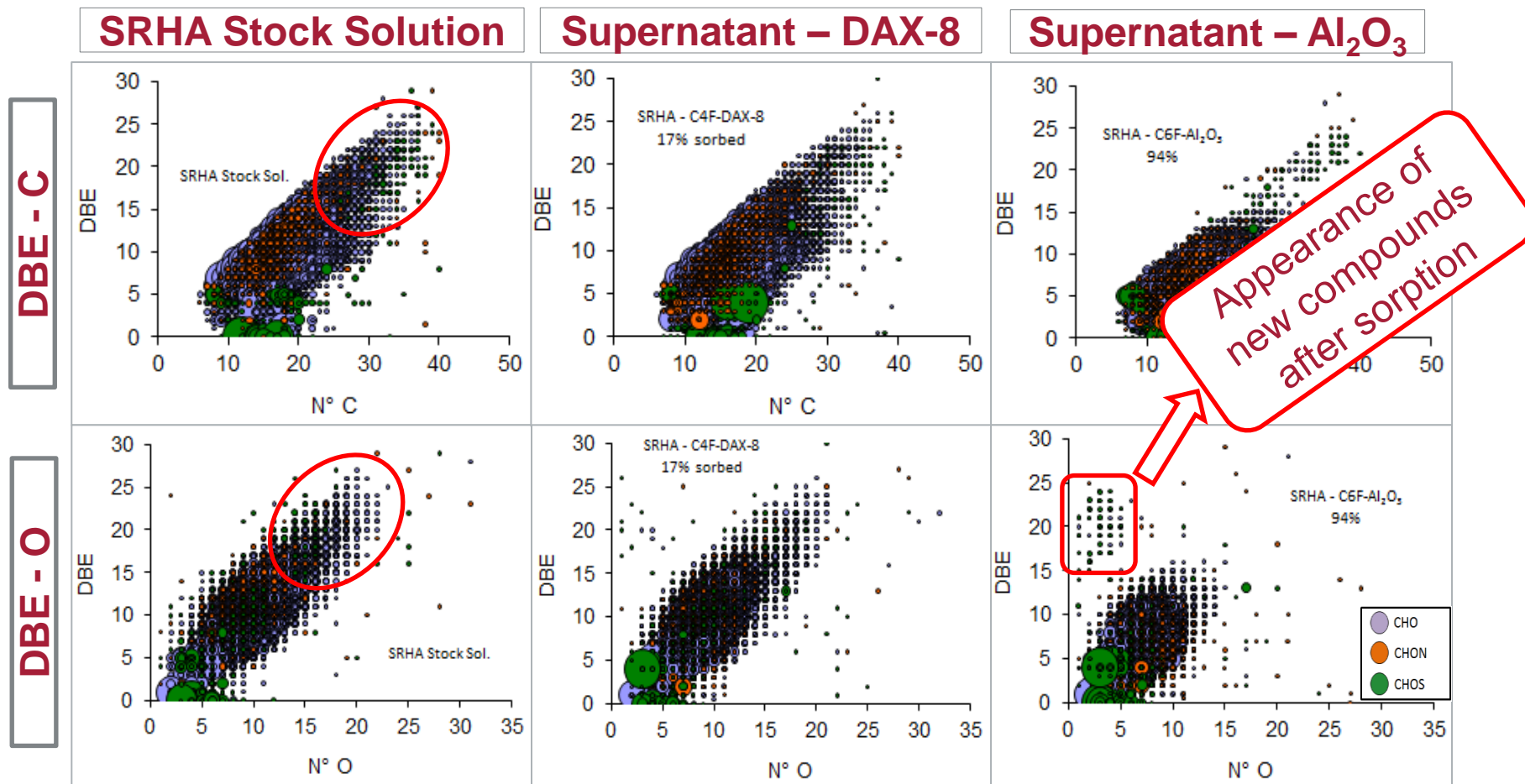
Sorption mechanism? → Al_2O_3 vs. DAX-8?



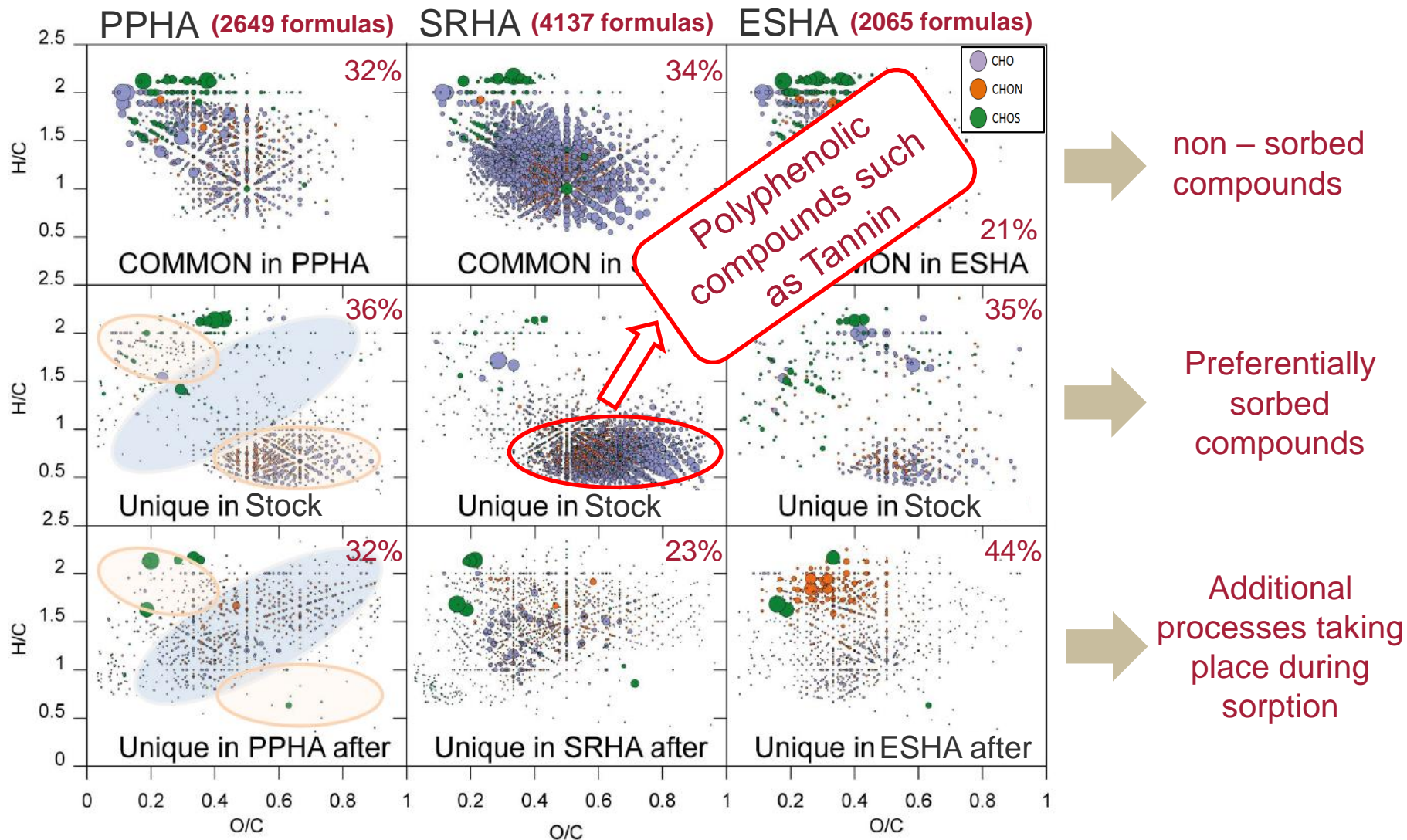
- Al_2O_3 : EDC suspension > EDC HA stock solution
- DAX-8: EDC suspension < EDC HA stock solution
- Above ~ 50% sorbed HA, EAC & EDC decreased in **supernatants**



FT-ICR mass spectrometry results



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





- **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 Al_2O_3 . 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).**



- **Dr. Michael Sander (ETH-Zurich) for great support and fruitful discussion on electrochemical set-up.**
- **Monika Hertel, Bernice Nisch, Ellen Struve (Uni. Tübingen).**
- **Sharmishtha Jindal and Michael Trumpp for experimental support.**

Thanks for your attention!