Spectral Induced Polarization Signatures of Biochar

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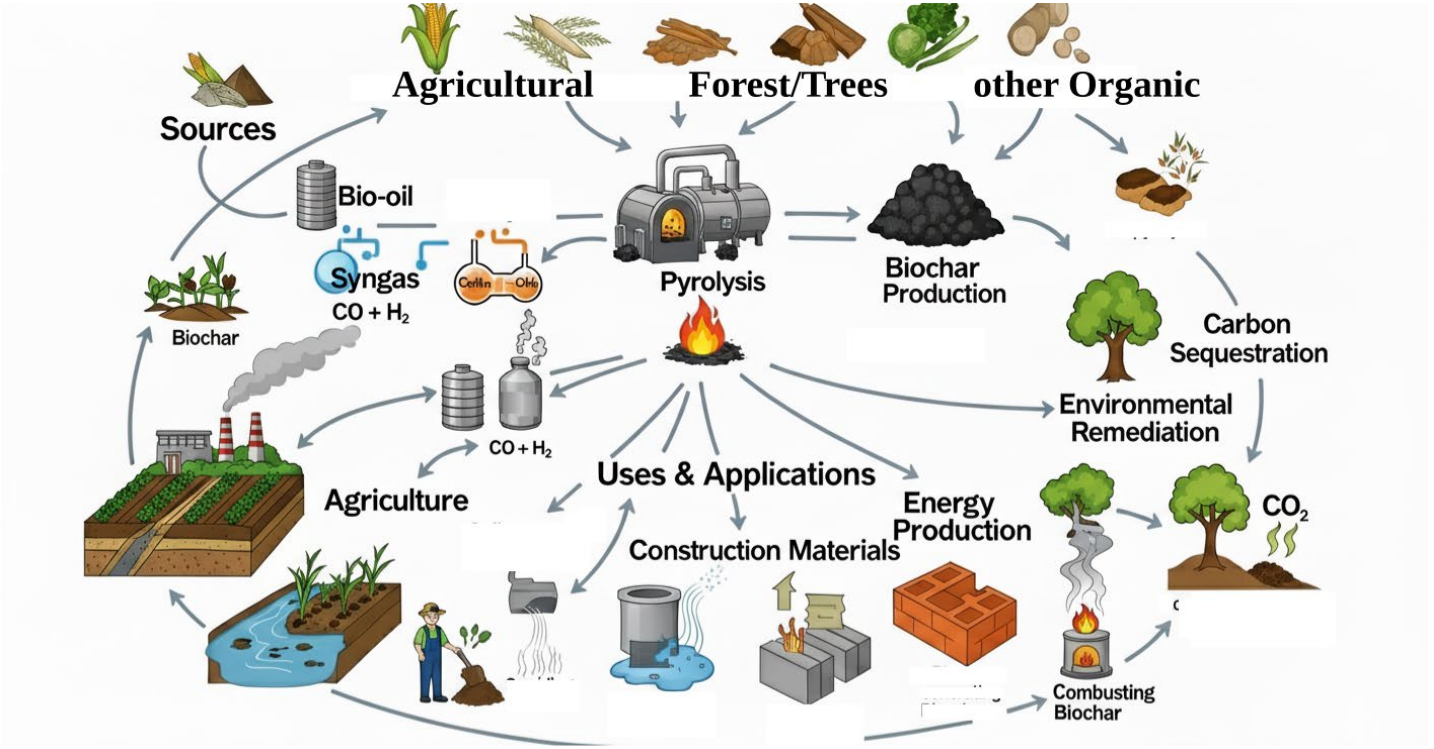
Biochar

Versatile & Environmentally Friendly

- Carbon rich product
- Biomass pyrolysis under oxygen-free conditions
- Sources:
  - Woody Biomass & Forestry Residues
  - Agricultural Crop Residues
  - Animal Manures & Waste
  - Other Organic Waste
    - treated sewage sludge
    - Food processing waste
    - Yard trimmings
    - Papermill sludge



Potential Benefits

Production

- heat, oil, and gas generation
- lock carbon in soil.
- greenhouse gas emission reduction

Improving Soil

- Increases soil fertility, water-holding capacity, cation exchange capacity, and soil microbial activity,
  - increased crop yield.
- Increases the efficiency of fertilizer use, decreases nutrient runoff, and binds to contaminants.
  - High-ash biomasses, higher pH values and cation exchange capacities
    - suitable for the sorption of metals in soils.

Transforming Waste

- Active management of biodegradable waste (agricultural, manure, forestry residues).
- Waste volume reduction / reduced environmental impact
- Remediation / management for a variety of contaminants (e.g. ,metals, organics, antibiotics).
- Engineered biochars (e.g. with iron) are designed to optimize their ability to immobilize contaminants (e.g. PRB)

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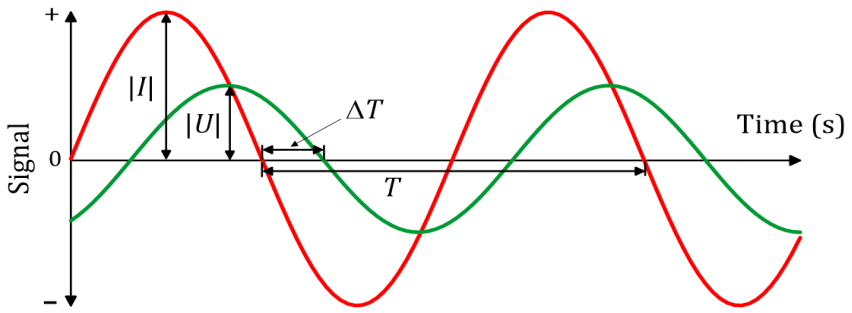
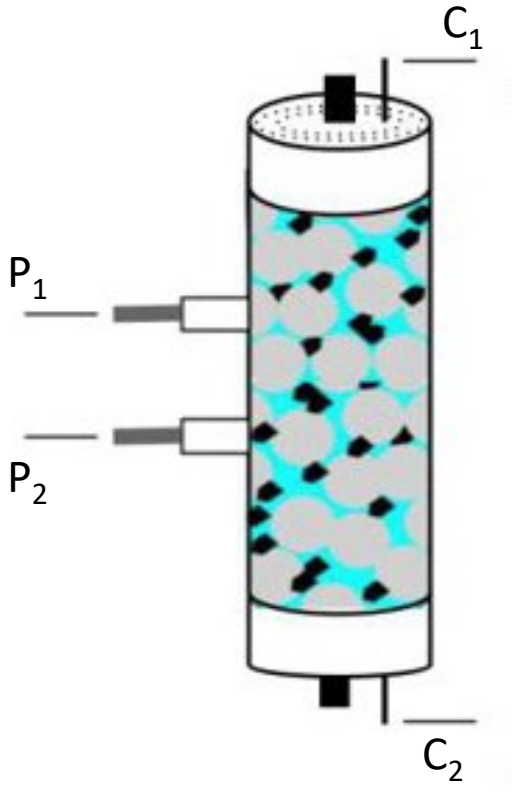
Spectral Induced Polarization

- Established geophysical method in mineral exploration
- Increased use in environmental applications
  - Characterization
  - Monitoring

- Sensitivity on interfaces
  - Solid phase/ fluid





Measured parameters

$$\varphi = \frac{2\pi\Delta T}{T} \quad |Z| = \frac{|U|}{|I|}$$

SIP Parameters

$$\sigma' = |\sigma|\cos(\varphi) \quad \sigma'' = |\sigma|\sin(\varphi)$$

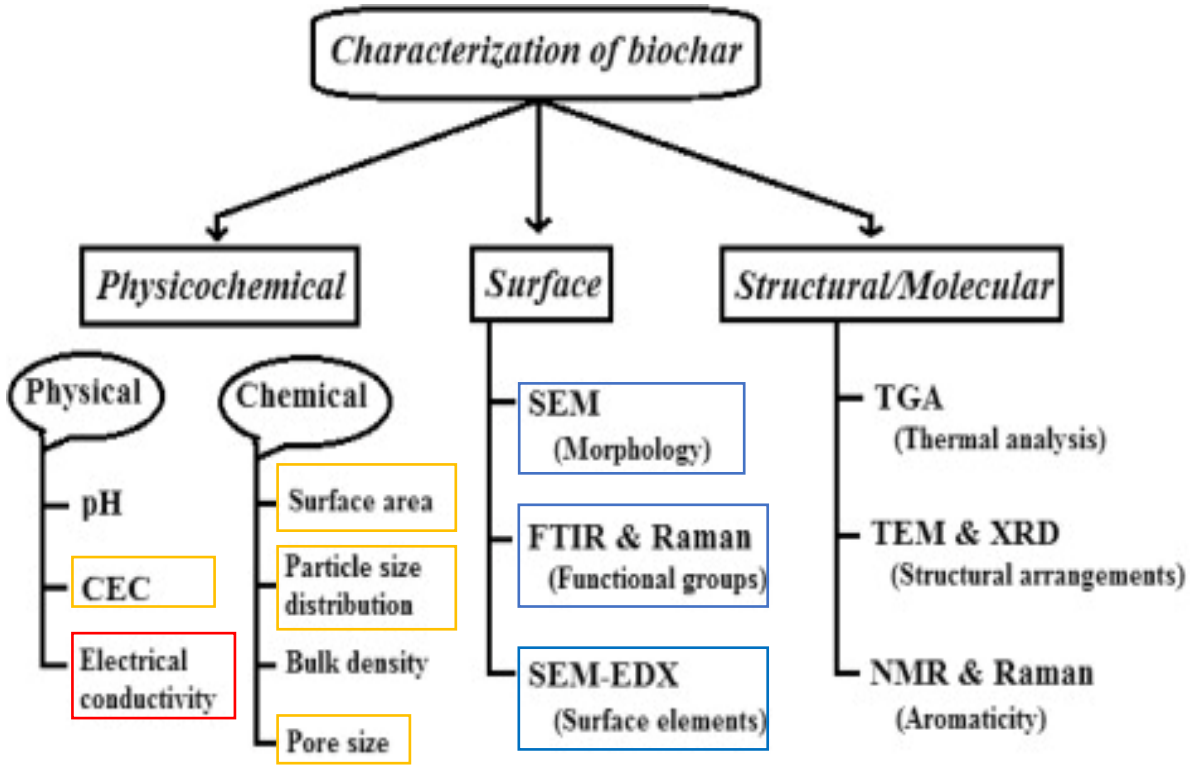
$$\sigma^* = |\sigma|e^{i\varphi}$$

$$|\sigma| = \frac{1}{K \times |Z|} = \sqrt{\sigma'^2 + \sigma''^2}$$

σ' is conduction (energy loss)
σ'' is polarization (energy storage)

Energy storage is only related to interfacial polarization

Why SIP?



* can be linked to IP parameters.
* can be obtained with IP measurements.
* can be used to support IP measurements.

Physicochemical, surface, and structural/molecular characterization of biochar (Yaashikaa et al., 2020).

Property / Process	SIP relevance	Biochar relevance
Surface area	Quantitative links	Increase with residence time pyrolysis T (and carbon content)
Contaminant remediation	Links to sequestration, precipitation, dissolution, degradation, sorption, surface interaction	Adsorption of metals (heavy, race); pesticides, organics (PAHs, PCBs, chlorinated), dyes
Biofilm/biominerals	Qualitative links to biofilm, cells, cell attachment; Quantitative?	Enhance anaerobic digestion through microbial activity, electron transfer, stability, inhibitor control (e.g. ammonia removal)
Cation Exchance Capacity (CEC)	Qualitative and quantitative links	Enhances soil properties (e.g. nutrient retention), remediation (e.g. contaminant immobilization), long term stability. Depends on pyrolysis T, feedstock, activation
Resolution	Hight spatial / temporal	Inhomogeneity issues can be very detrimental to soil/environmental application.

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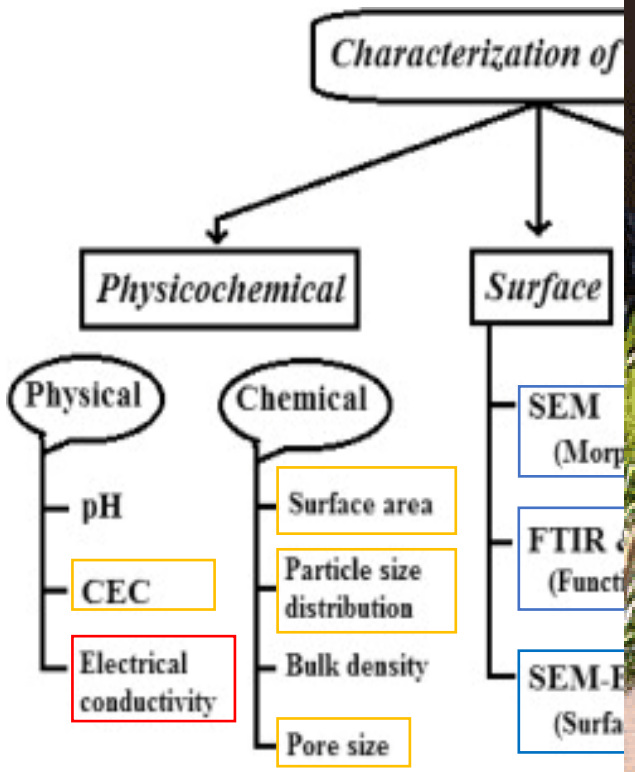
Why SIP?



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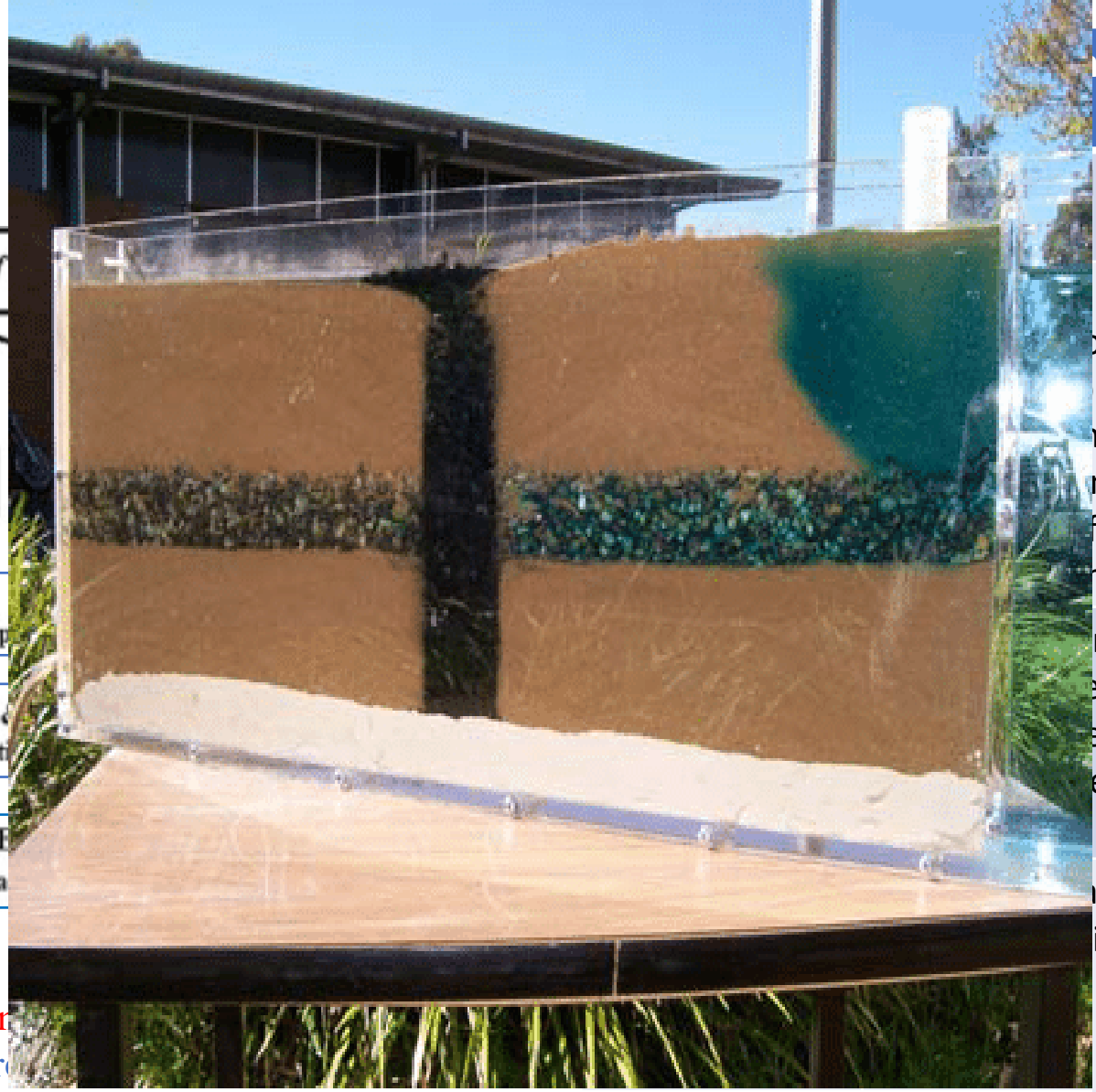
Physicochemical, surface, and structural/mo



Demo of biochar filled trench: A permeable Reactive Barrier for shallow groundwater remediation (Craig et. al, 2015).

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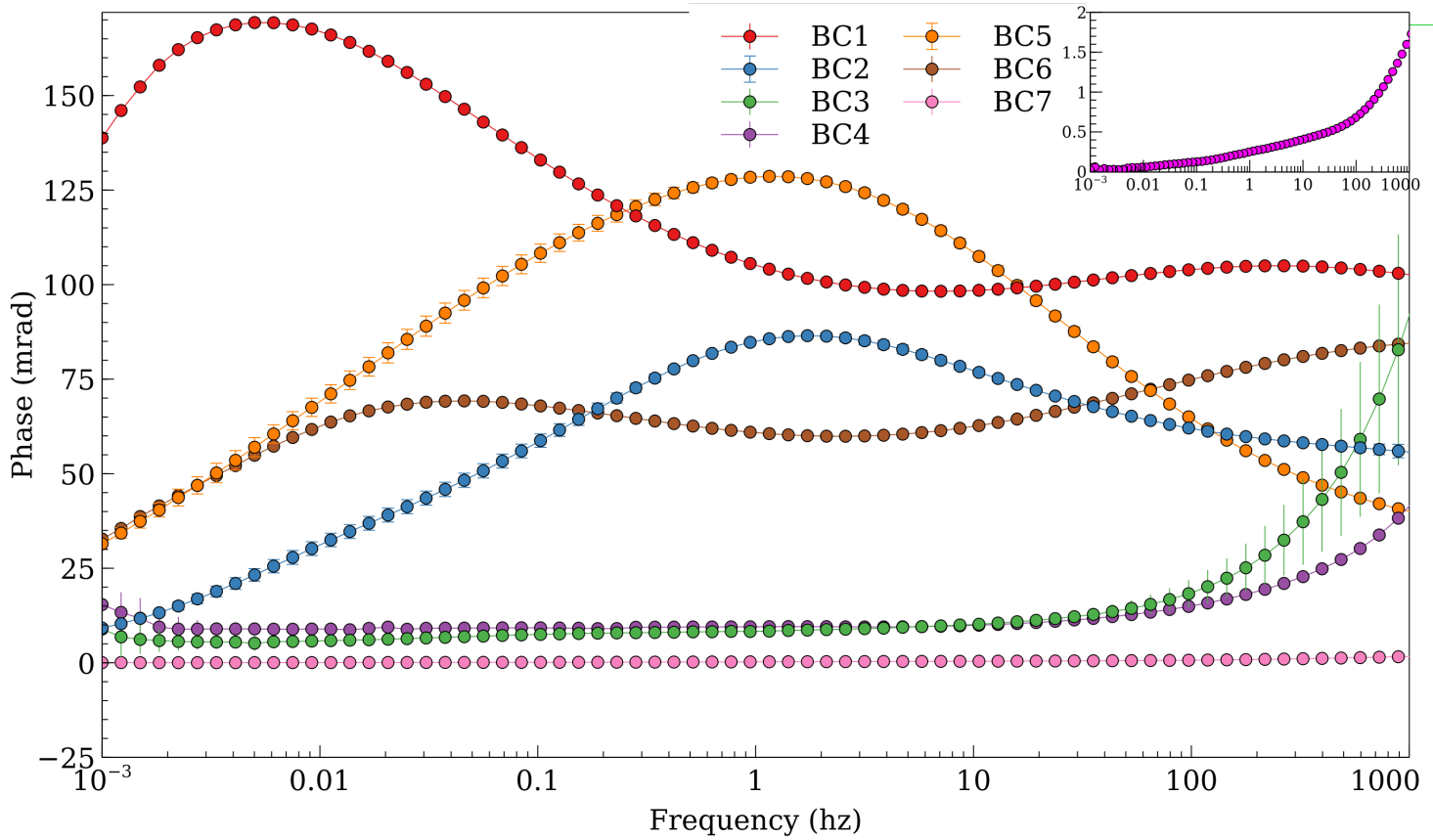
Biochar Samples	Pyrolysis Temperature (°C)	Raw Material	Carbon	SSA (m2/g)
BC1	1000	Wood	69%	423
BC2	500	Hardwood Woodchips	67%	148
BC3	450	Fir Wood Chips	72%	165
BC4	600-700	Nutshells	74%	202
BC5	800-900	Walnut Shells	69%	313
BC6	700	Wood Biochar, Softwood Forestry Residues	37%	474
BC7	600	Ground Sugar Beet	62%	171

Carbon content & SSA

Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Heterogeneous (as used)
	Duplicate measurements



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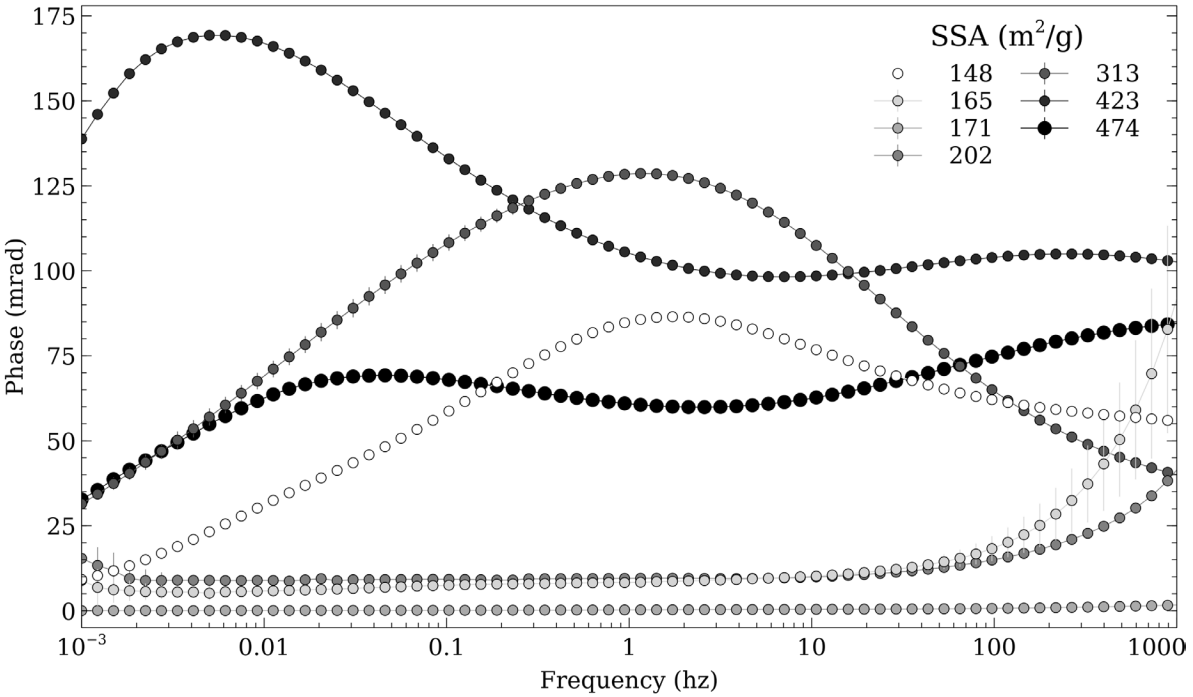

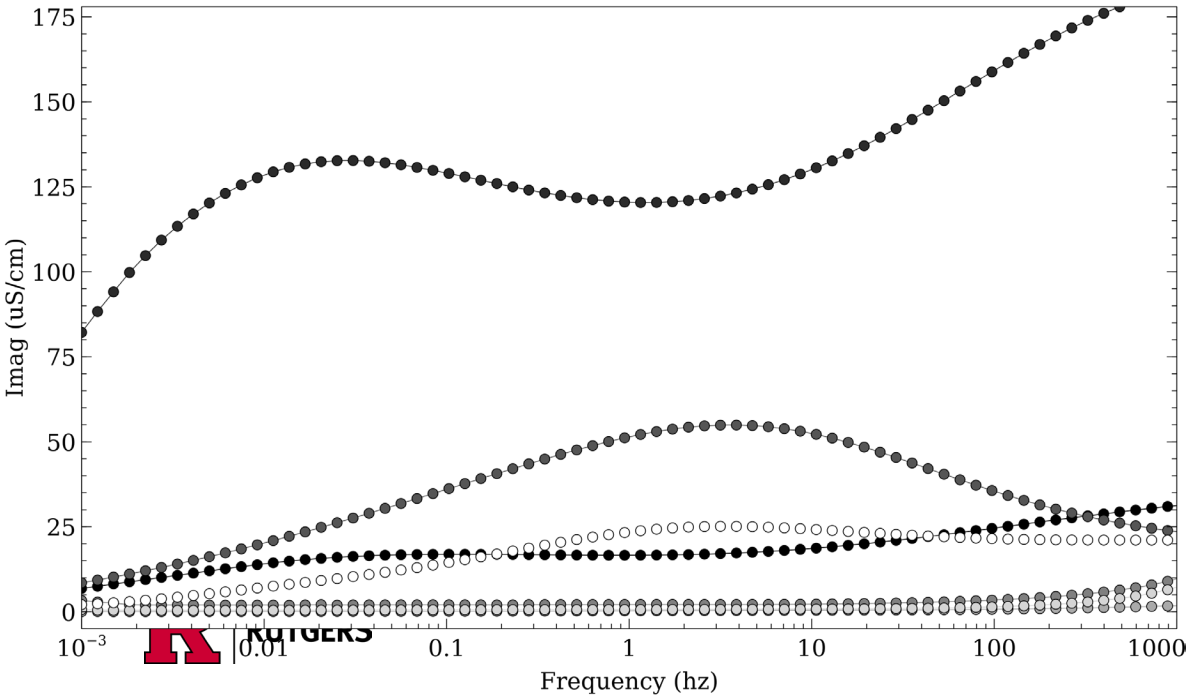

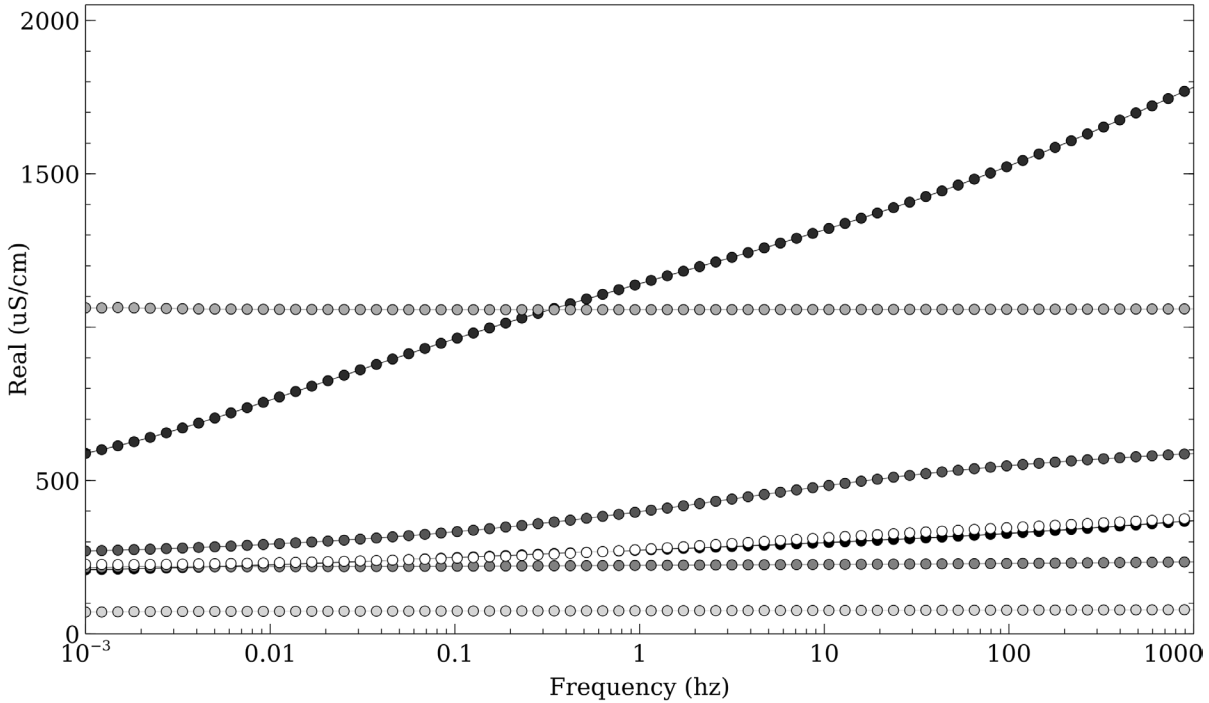

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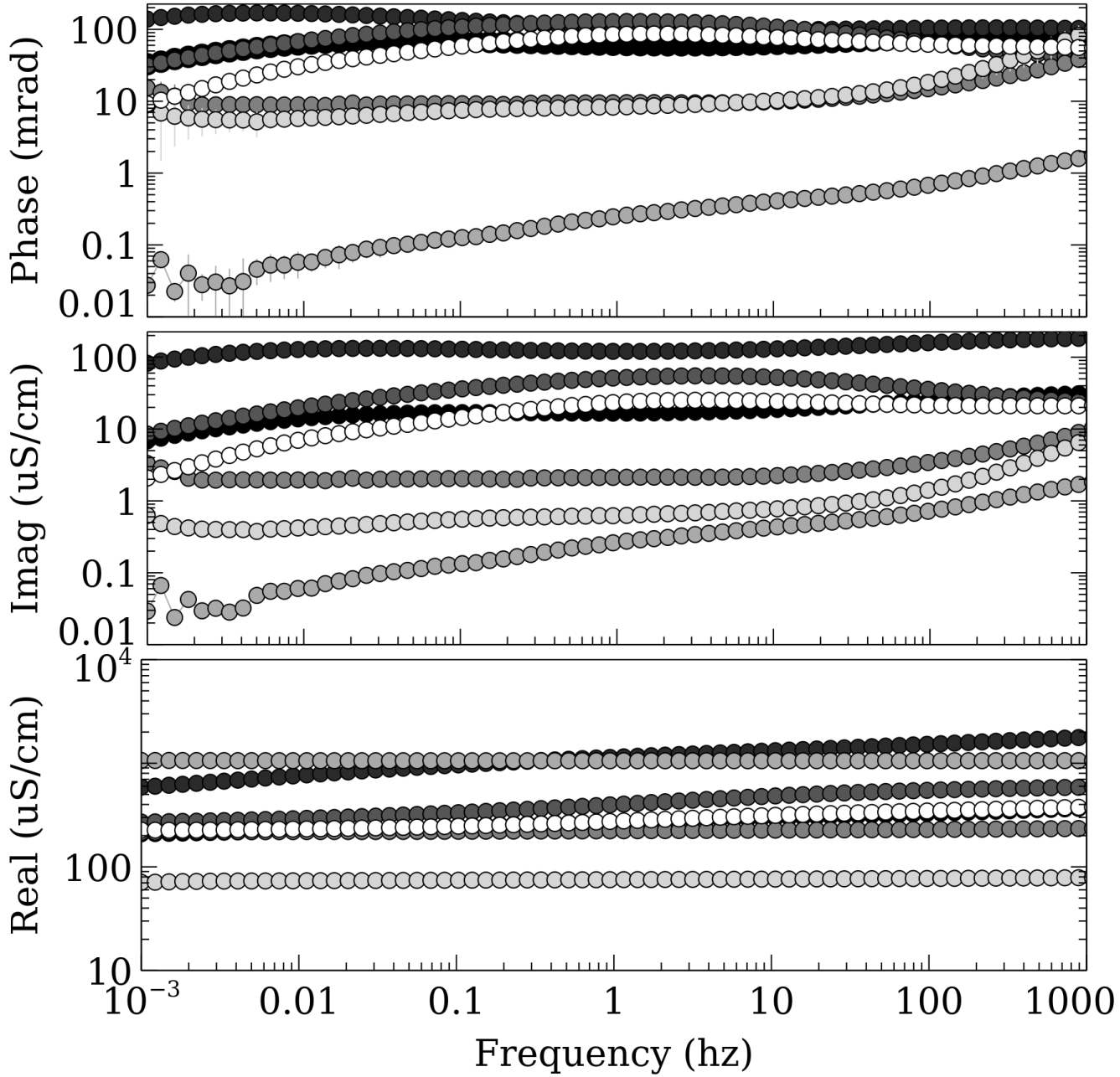

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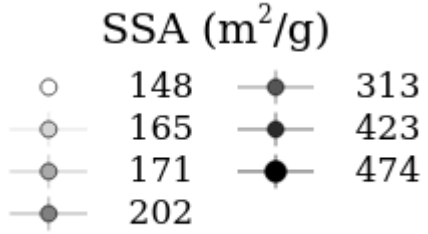

SIP advantage

Imag/phase better diagnostic property

- Large range
- Unique response

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Carbon content & SSA

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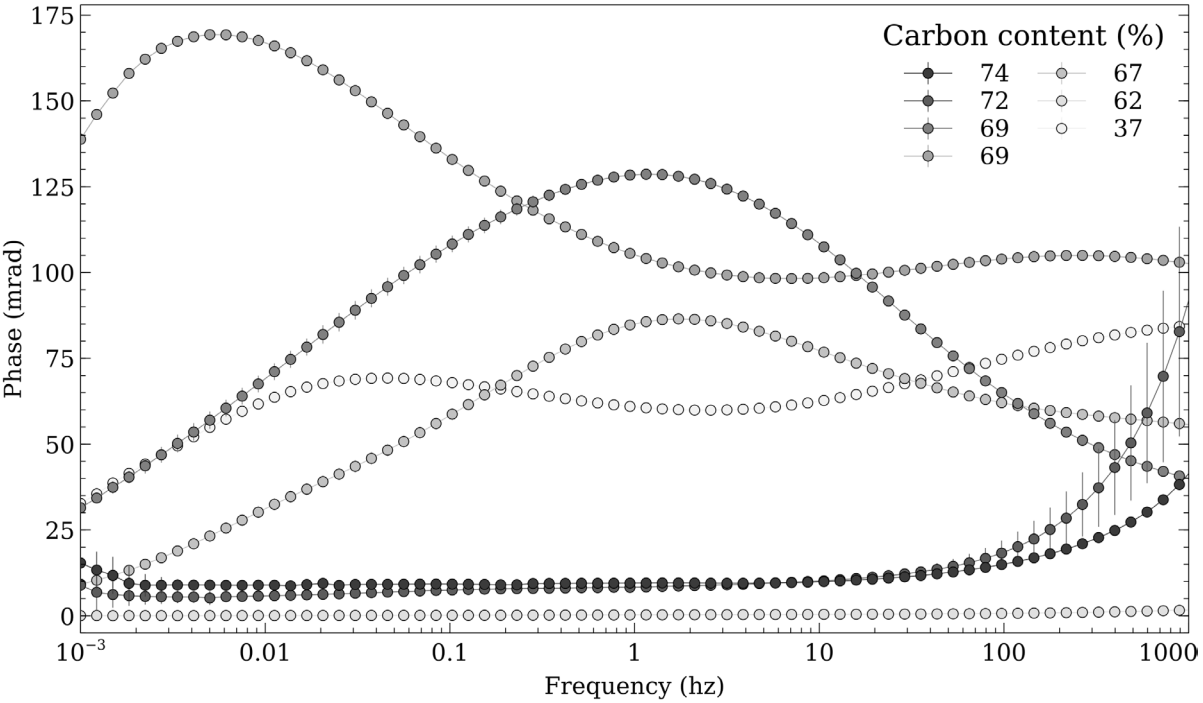
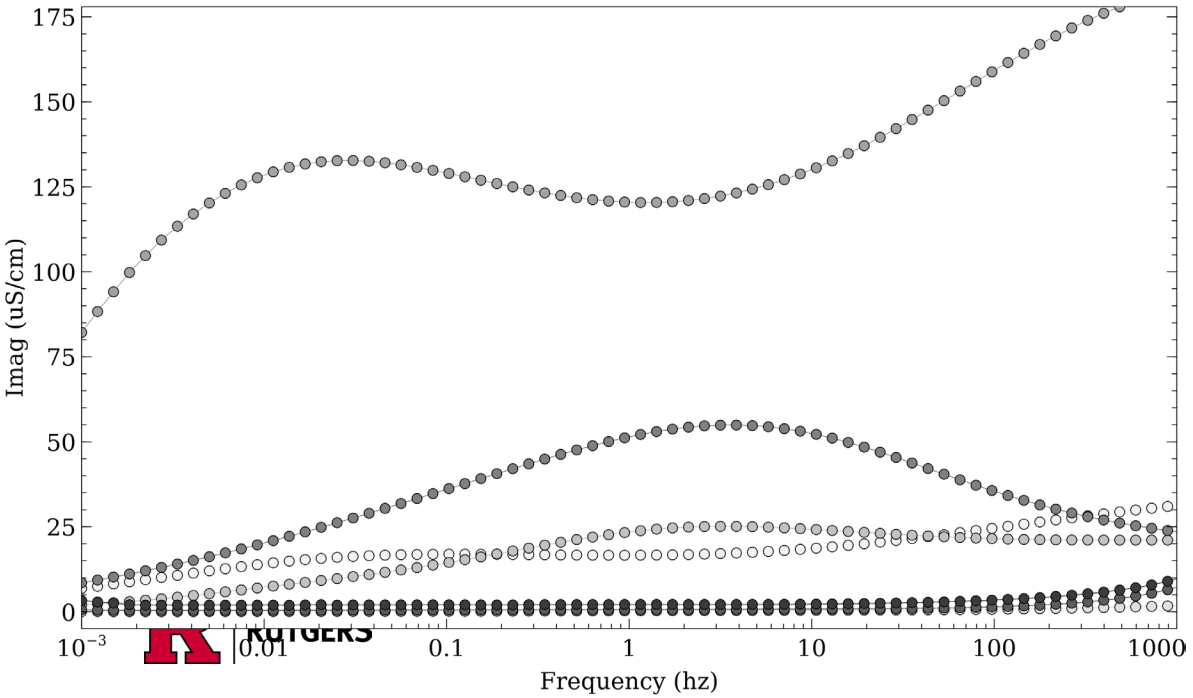
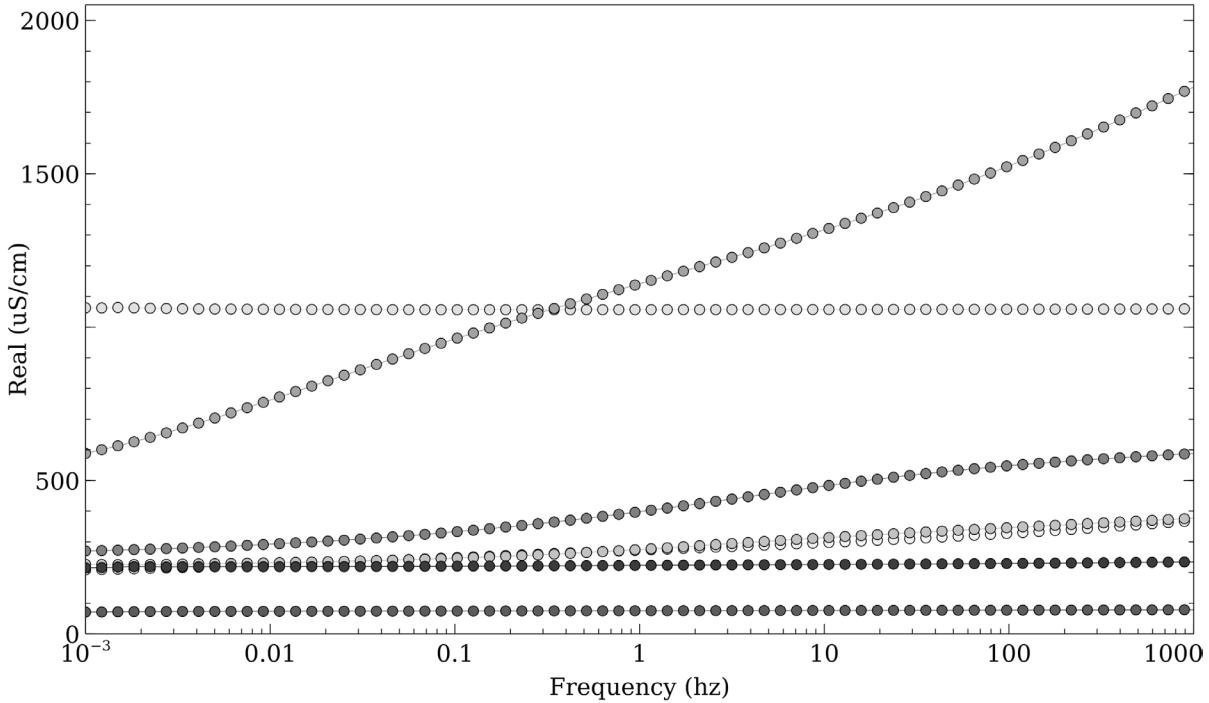
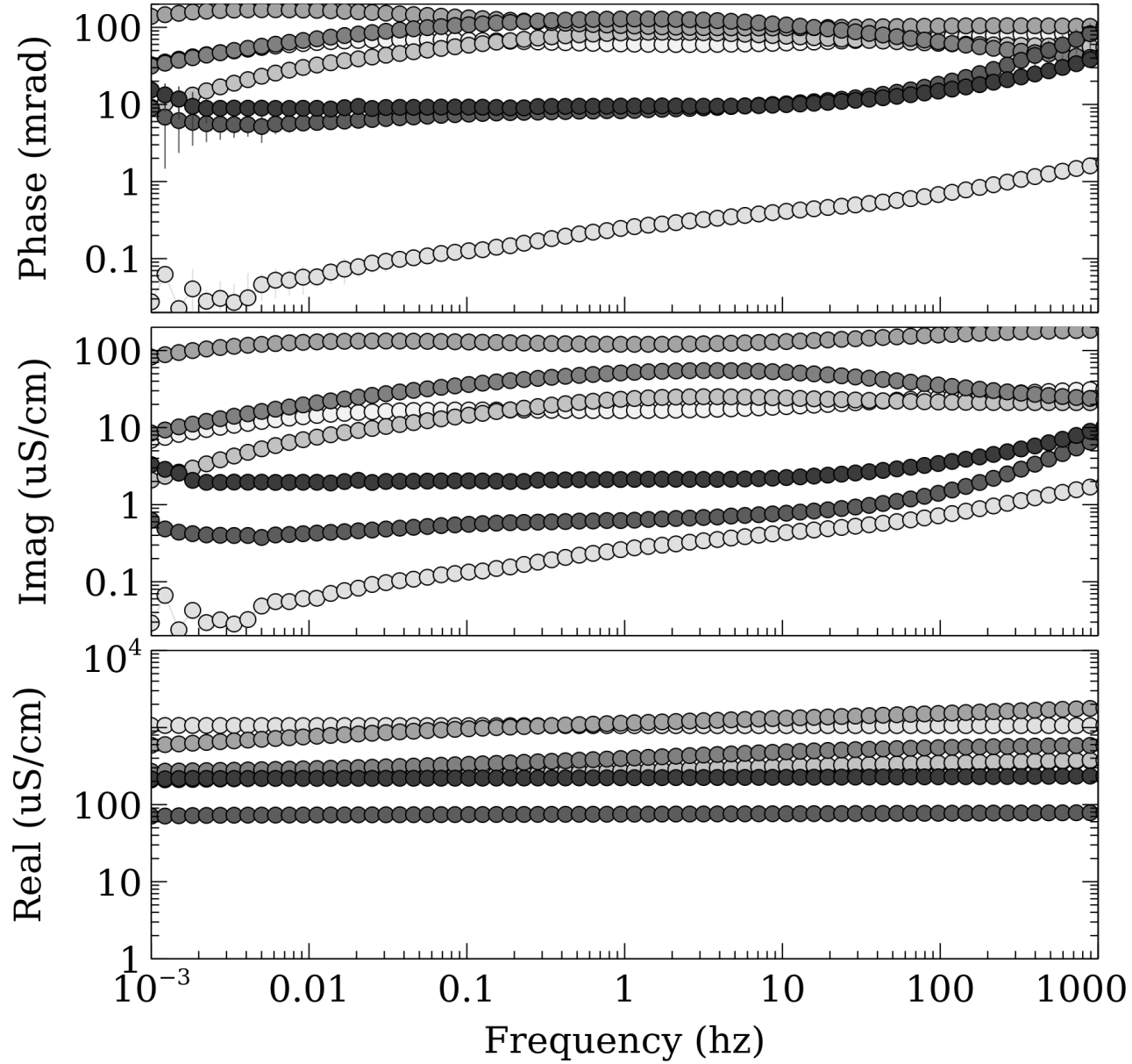






Carbon content & SSA



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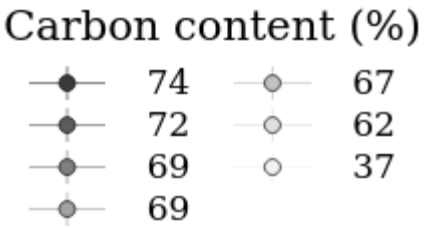

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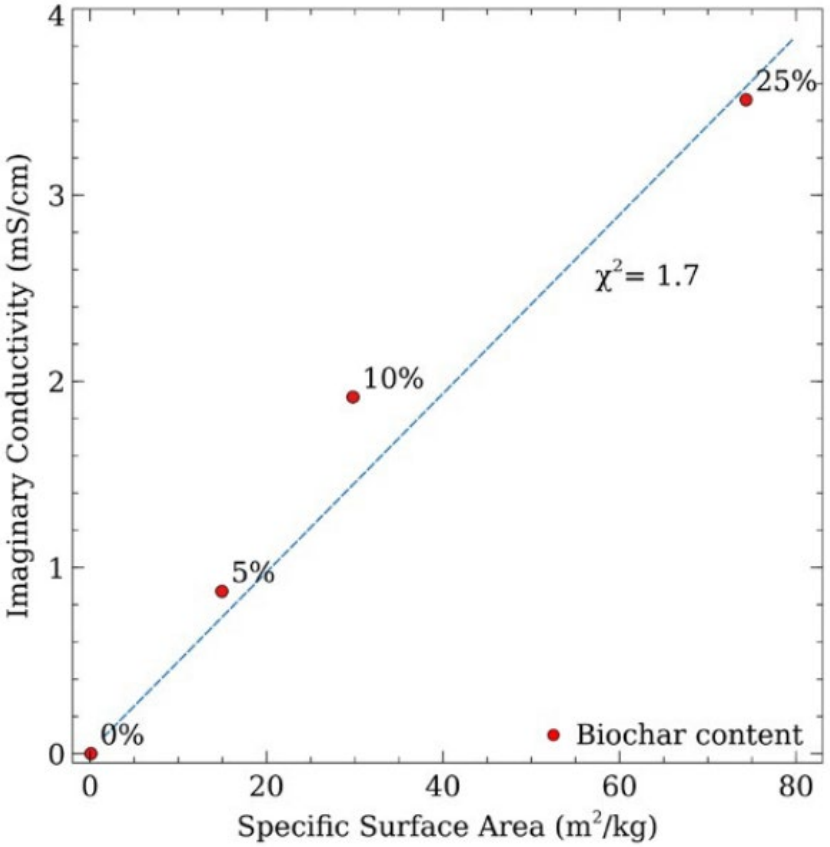

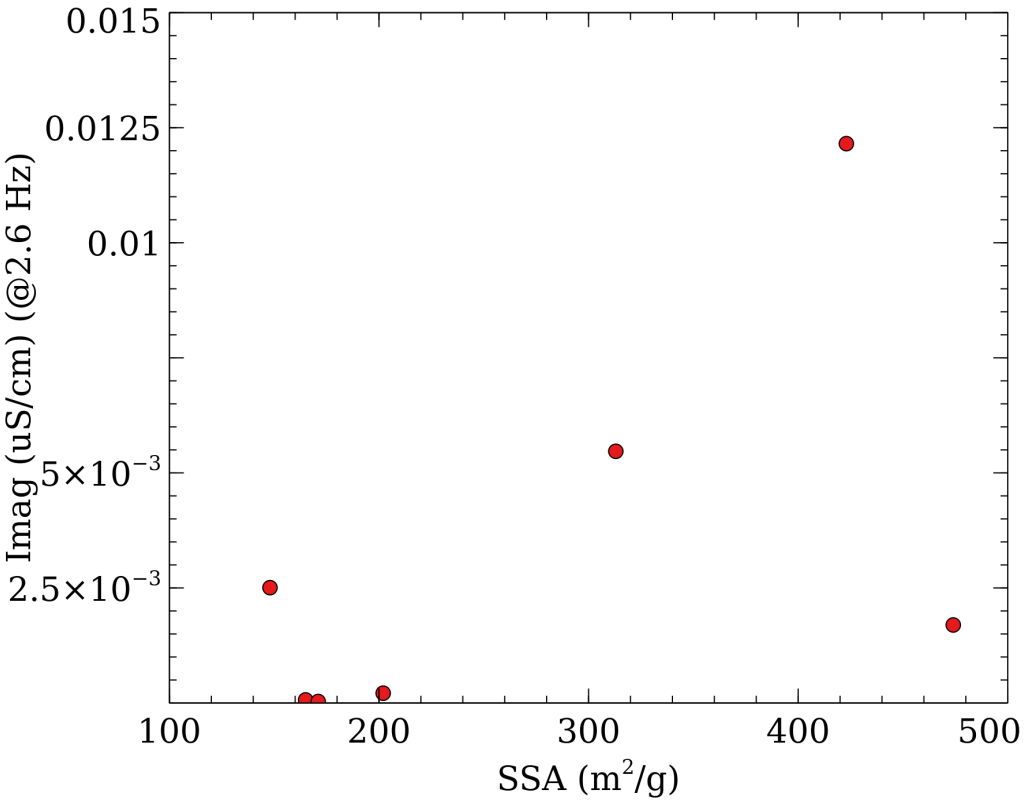

- Estimated total SSA
- Same biochar
- homogeneous grain size
- increased concentration)

Kirmizakis et al. (2019)

- Biochar only SSA
- Varied biochar
  - Varied grain size
  - Varied SSA
- same concentration

Kirmizakis et al. (2019)

Carbon content & SSA

Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Heterogeneous (as used)
	Duplicate measurements

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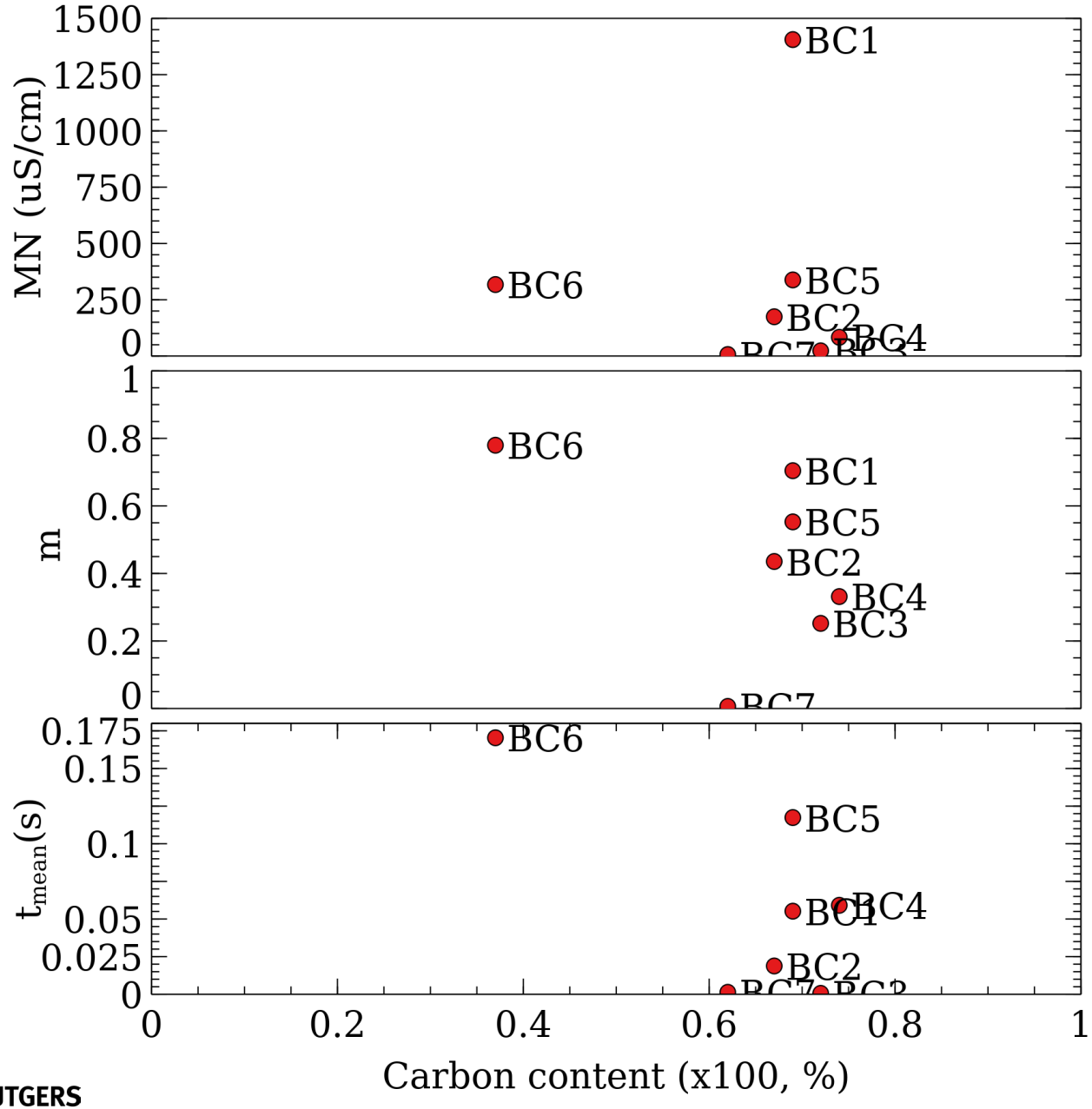
Carbon content & SSA



Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Heterogeneous (as used)
	Duplicate measurements

Debye Decomposition derived parameters

- 0.001 - 1000 Hz (fit range)
- Compared to carbon content
  - No obvious trend

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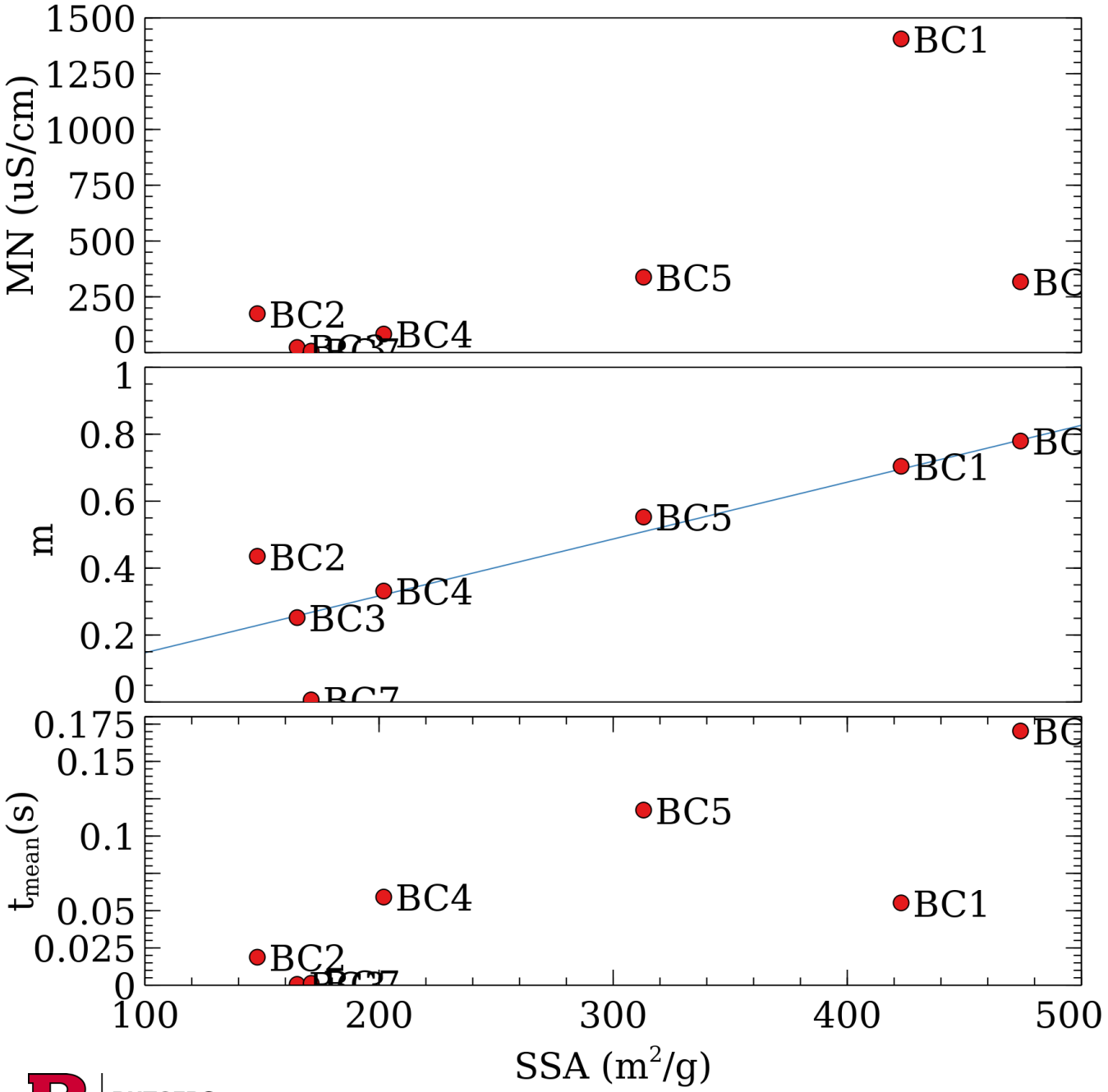
Carbon content & SSA



Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Heterogeneous (as used)
	Duplicate measurements

Debye Decomposition derived parameters

- 0.001 - 1000 Hz (fit range)
- Compared to surface area (SSA)
  - No strong trends
  - m shows linear trend in values > 200 m^2/g *

*SSA of the BC content only

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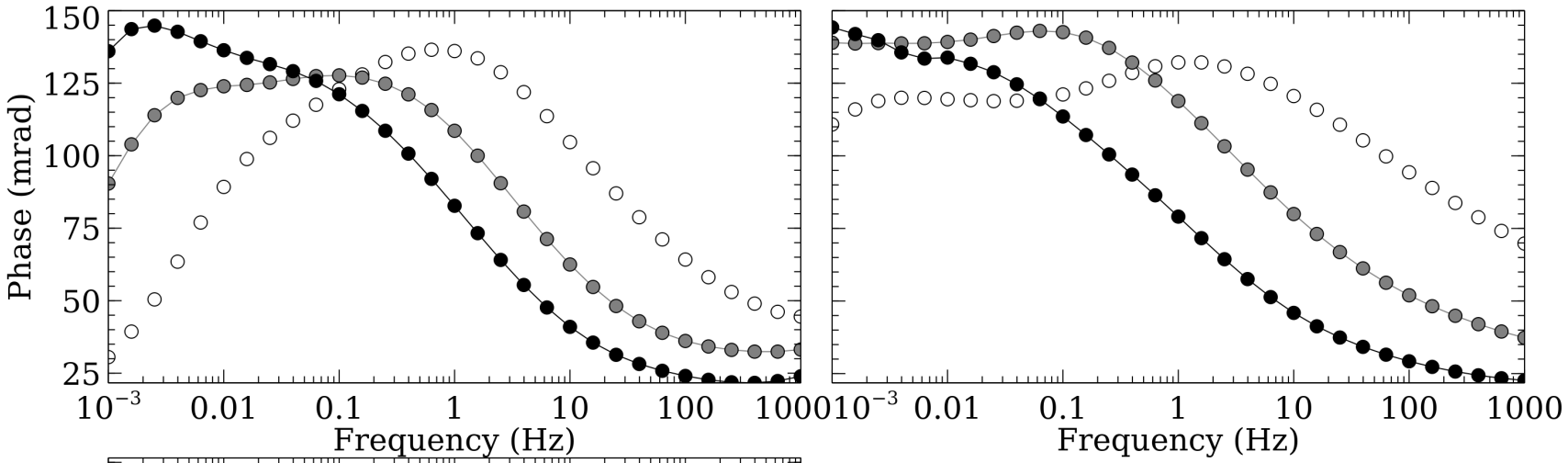
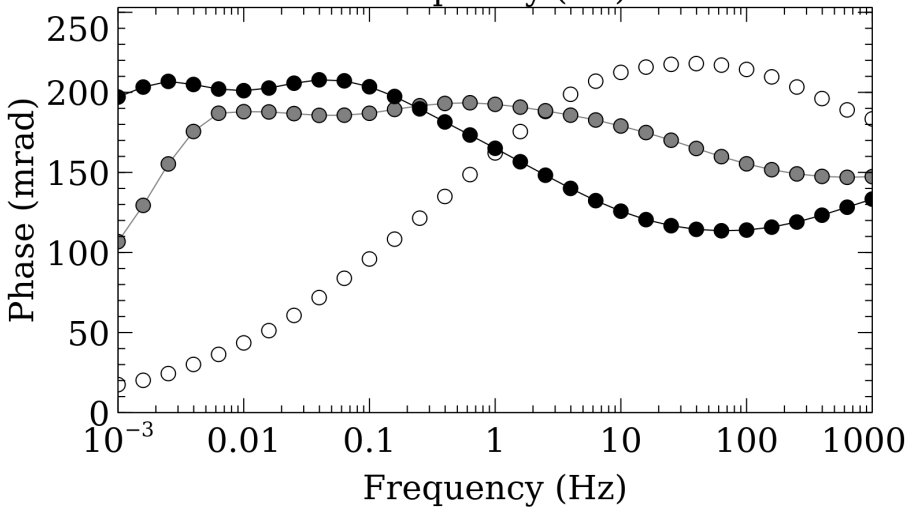
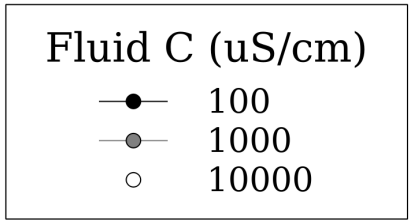
Salinity



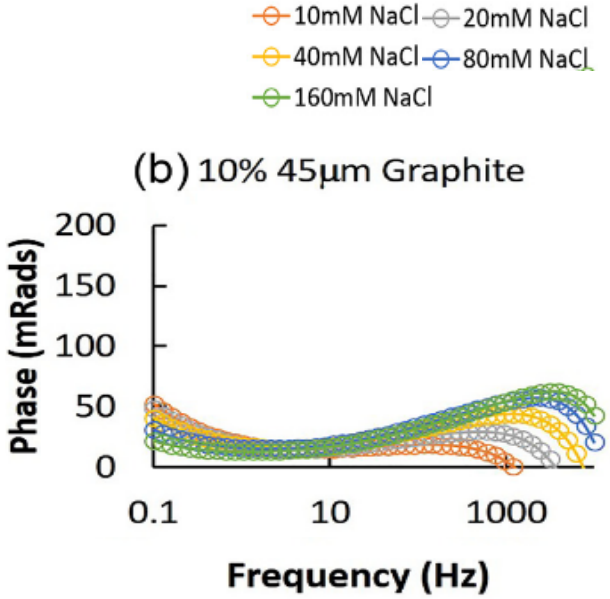




Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Heterogeneous (as used)
	Duplicate measurements
Similar CC*	Varied SSA
EC*	300-1100 uS/cm

- As provided by the vendor



- Peak frequency increases
- Peak magnitude ~ same
- Similar trend to graphite particles

Wu and Peruzzo (2020)

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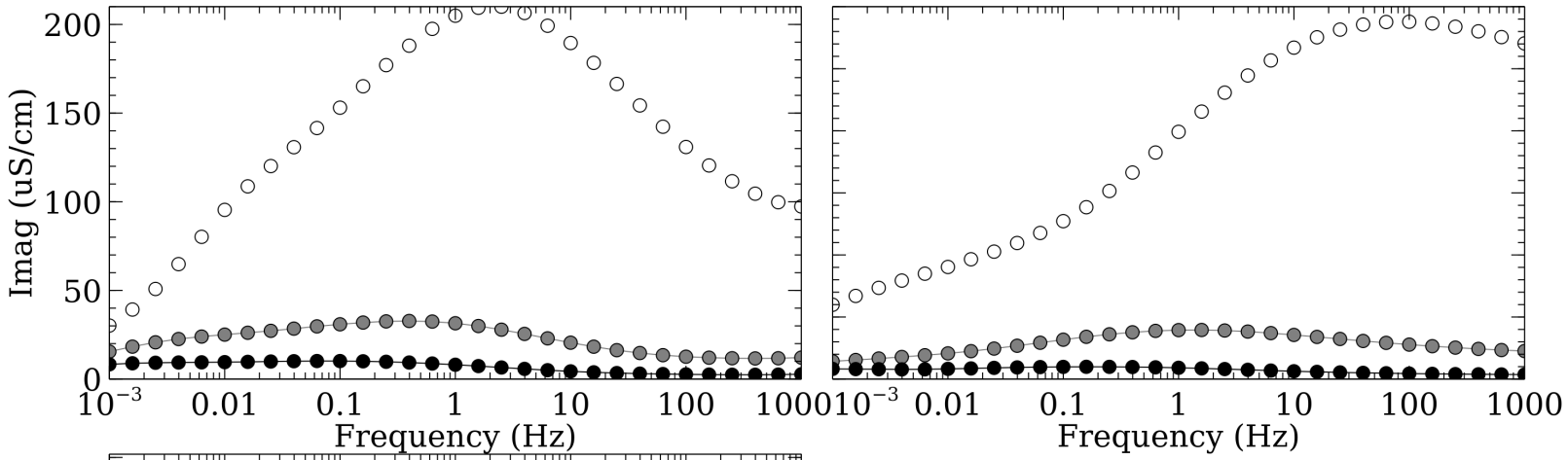
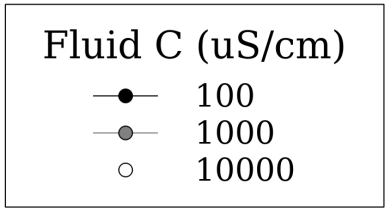
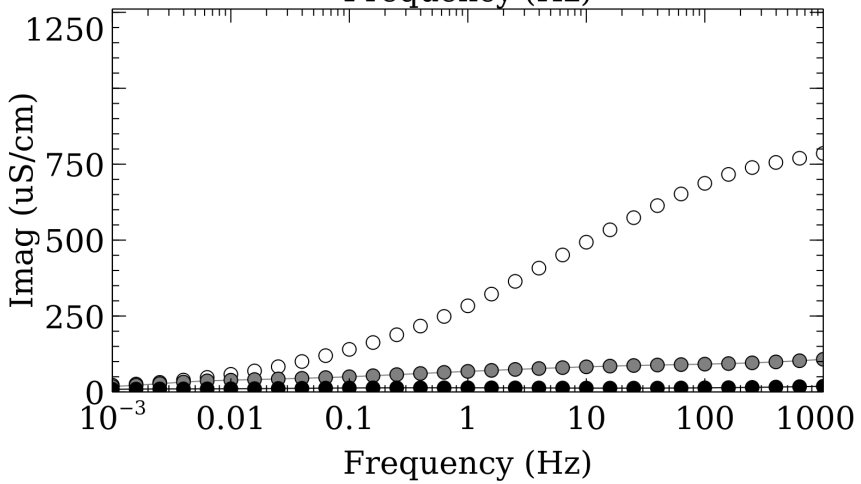
Salinity







- Peak frequency very small change
- Peak magnitude increase
- Similar trend to graphite particles

Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Heterogeneous (as used)
	Duplicate measurements
Similar CC*	Varied SSA
EC*	300-1100 uS/cm

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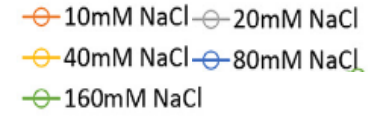

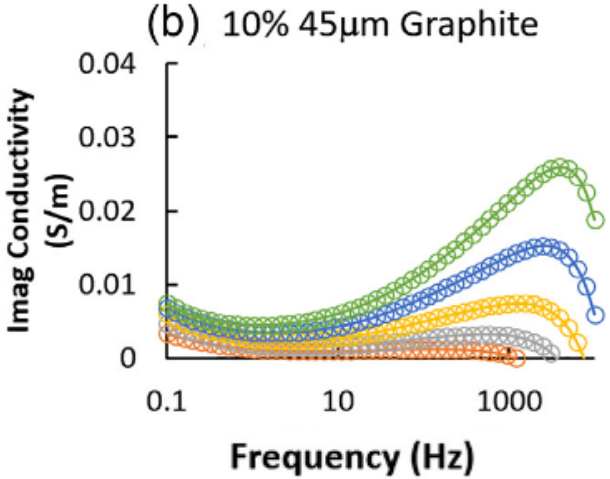

Wu and Peruzzo (2020)

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Salinity

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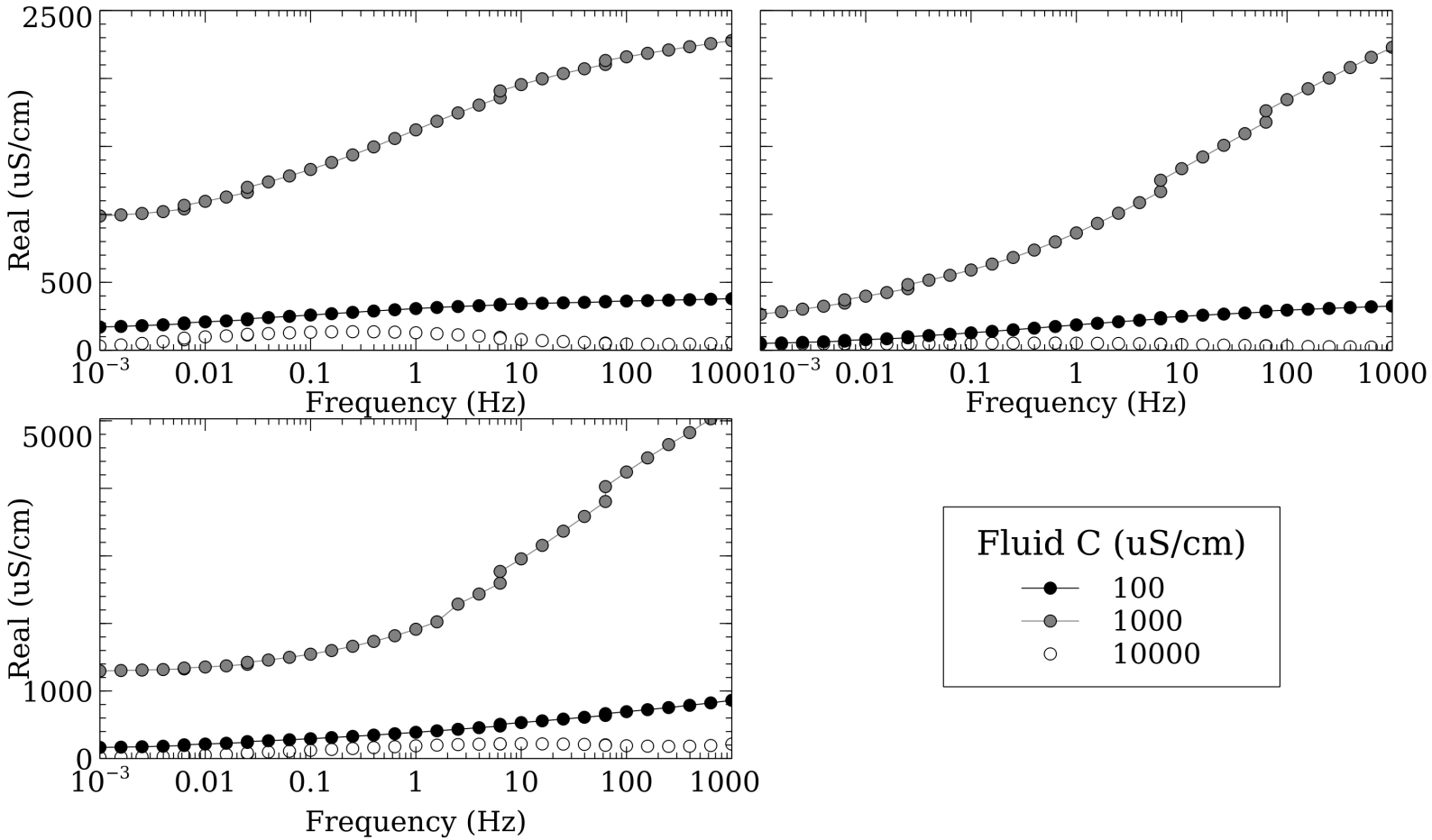

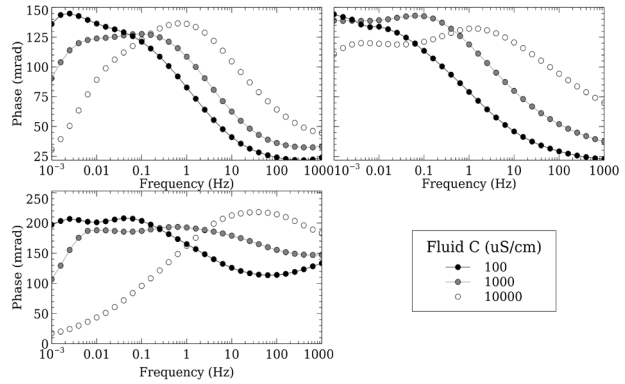

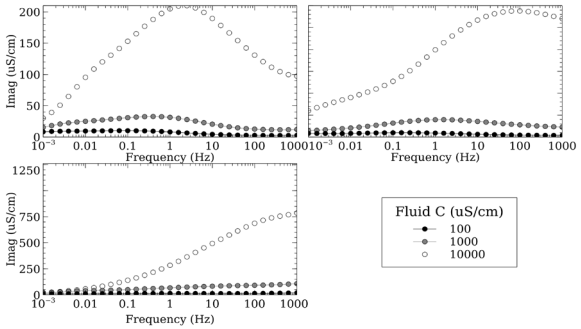

- Higher salinity – different behavior

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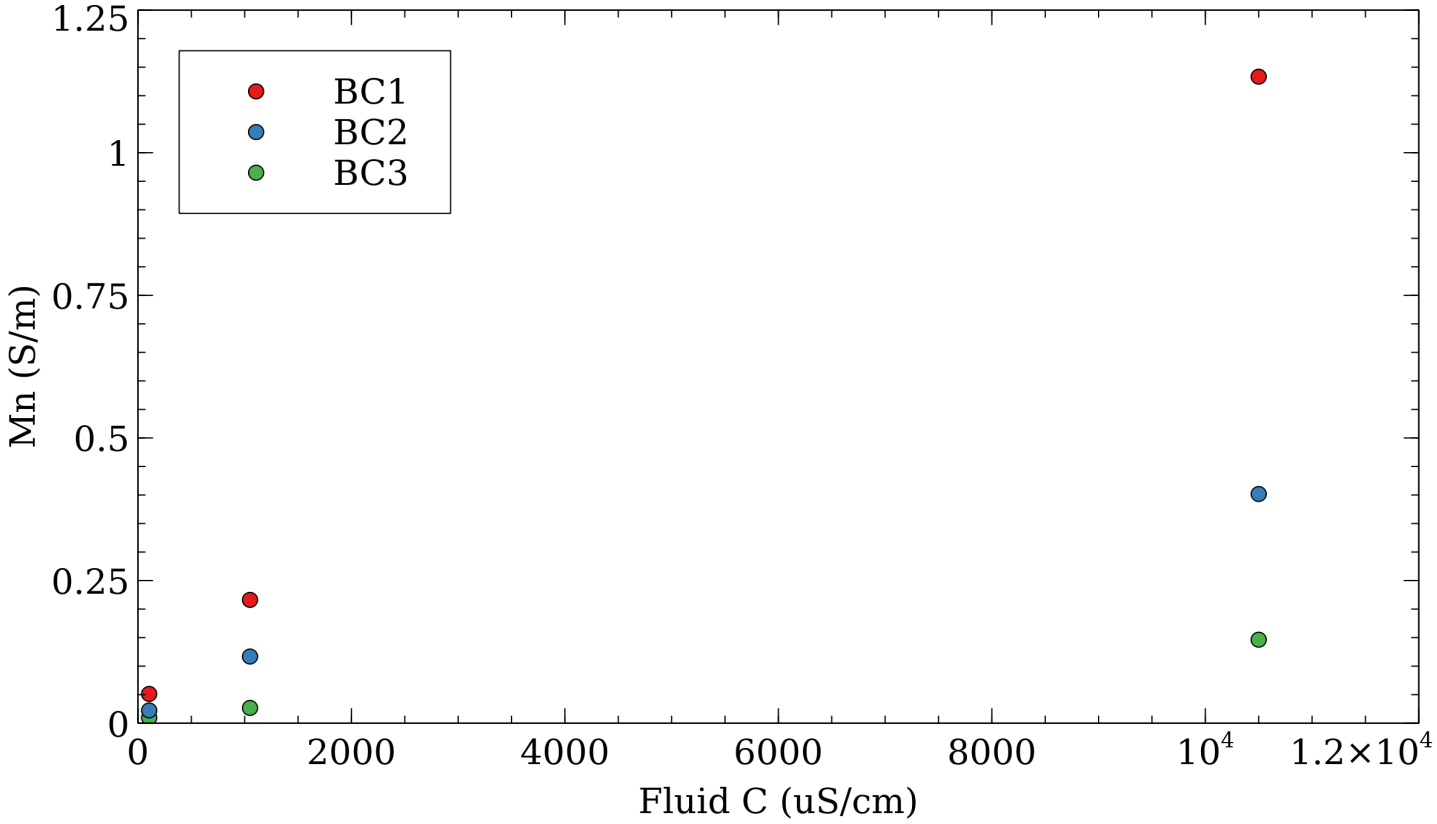
Salinity



- Mn is increasing with increasing fluid conductivity
- Similar behavior with dispersed metal particles

Experimental conditions

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	Duplicate measurements
Similar CC*	Varied SSA

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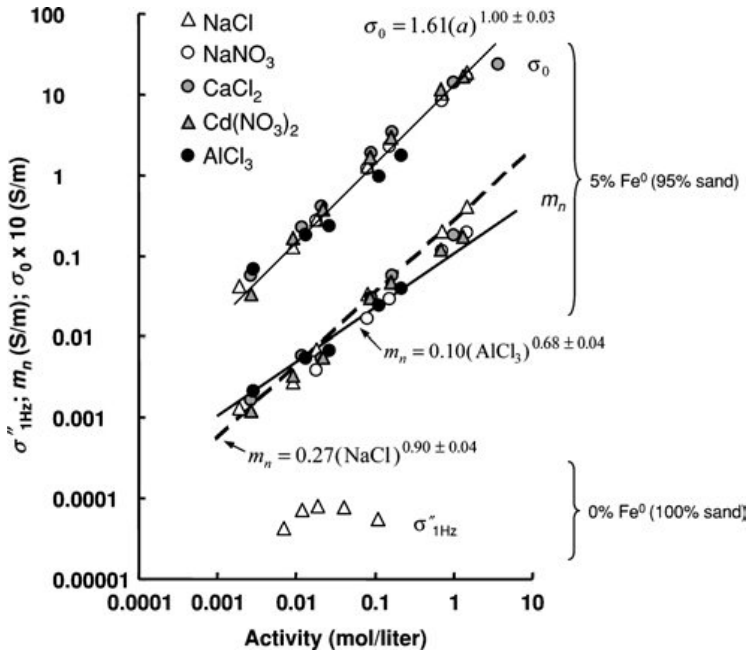

M_n Vs electrolyte activity (Slater et al., 2005)

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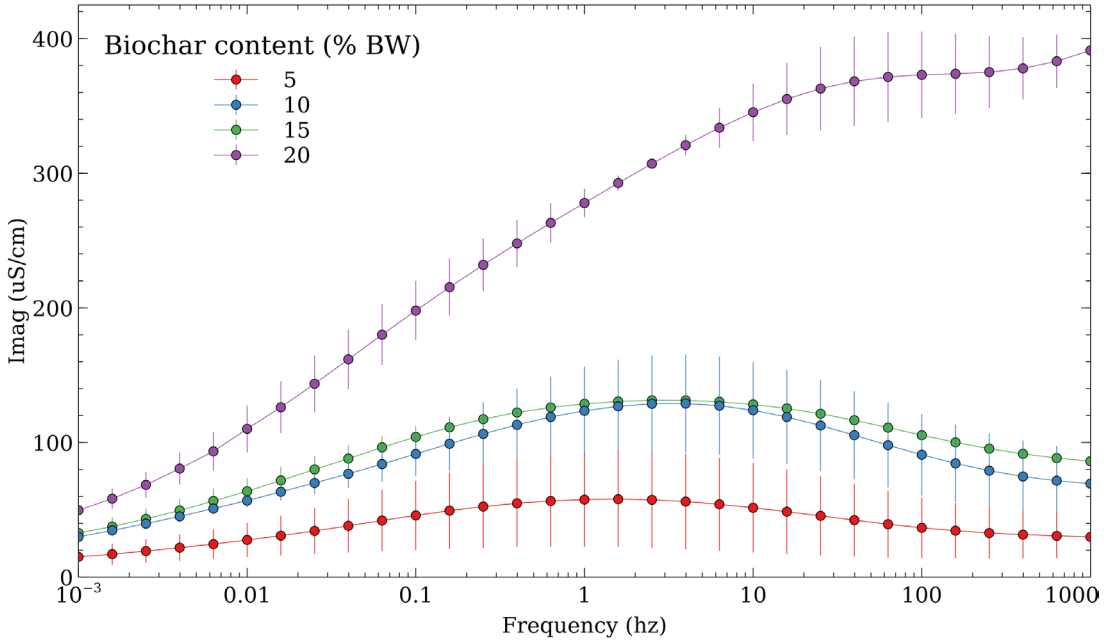

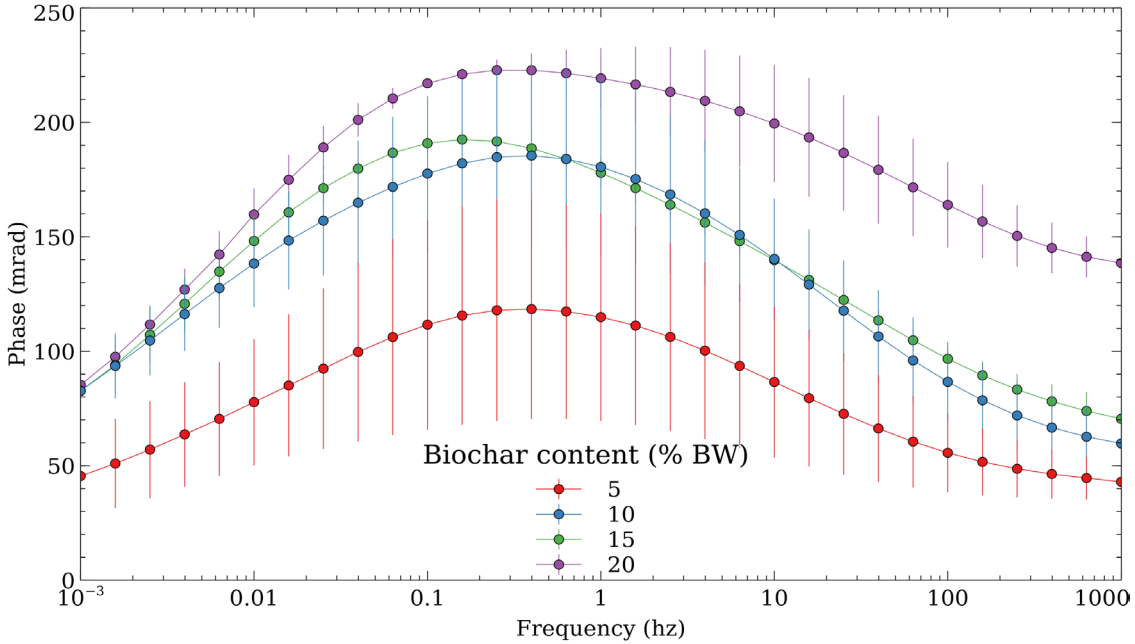

- After certain concentration behavior changes
- Impact of the geometric arrangement of particles

Concentration

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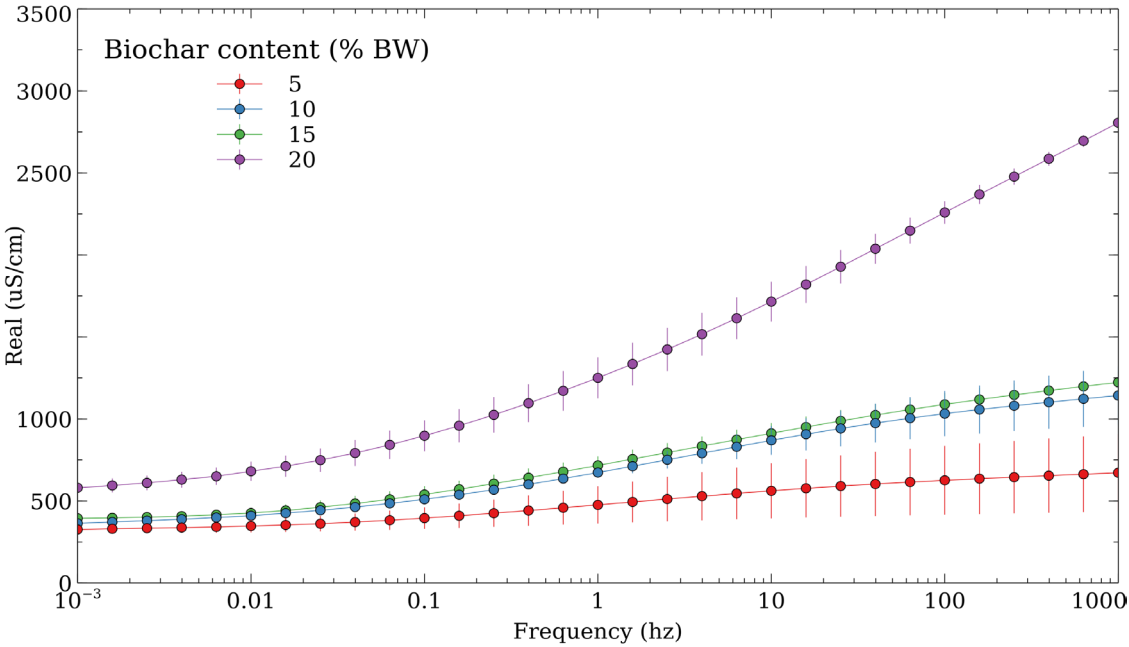
	Duplicate measurements



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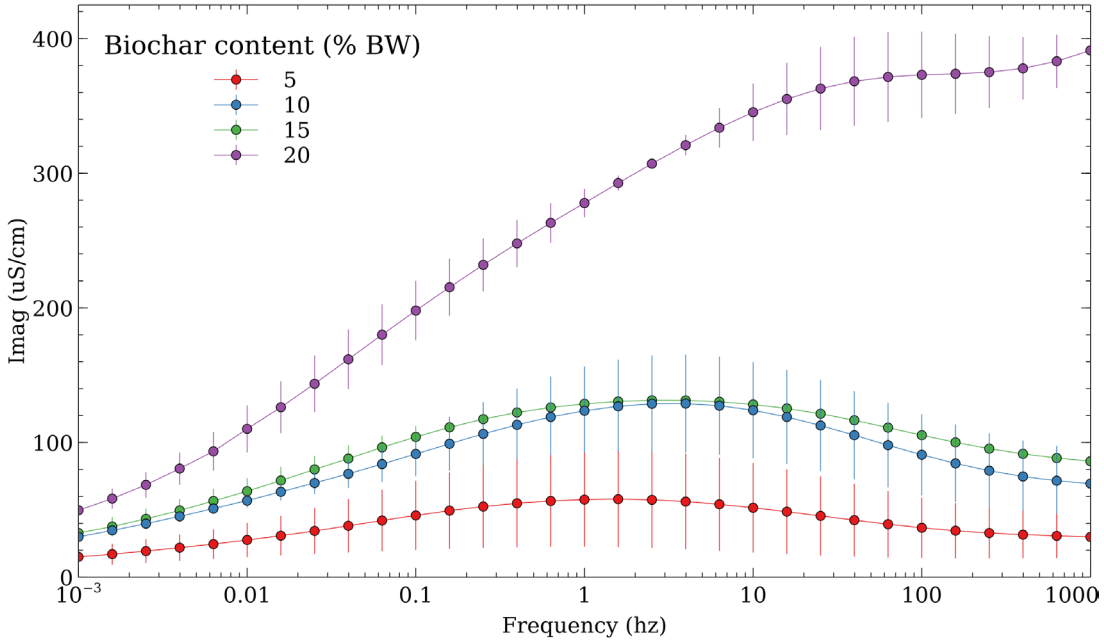

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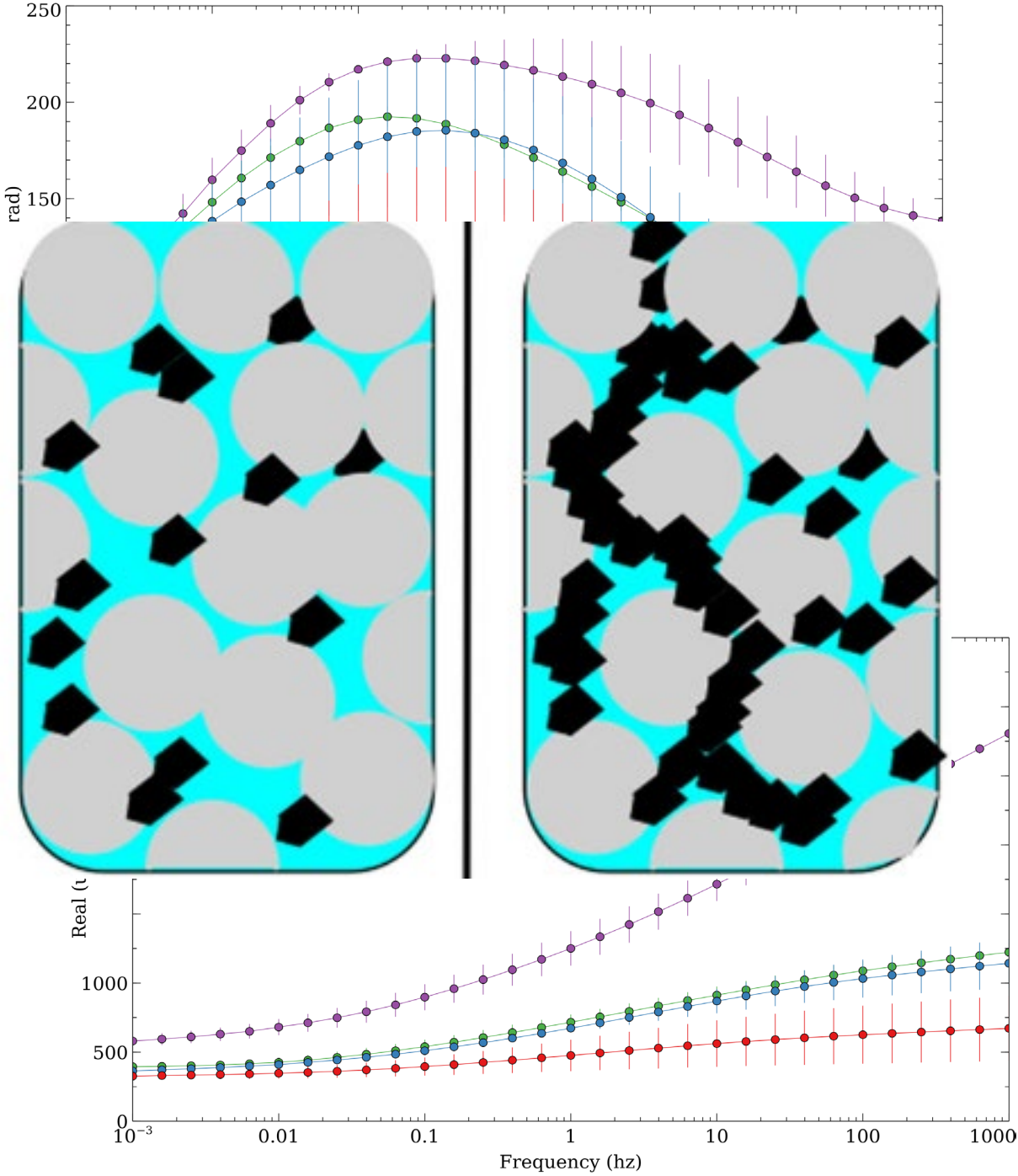

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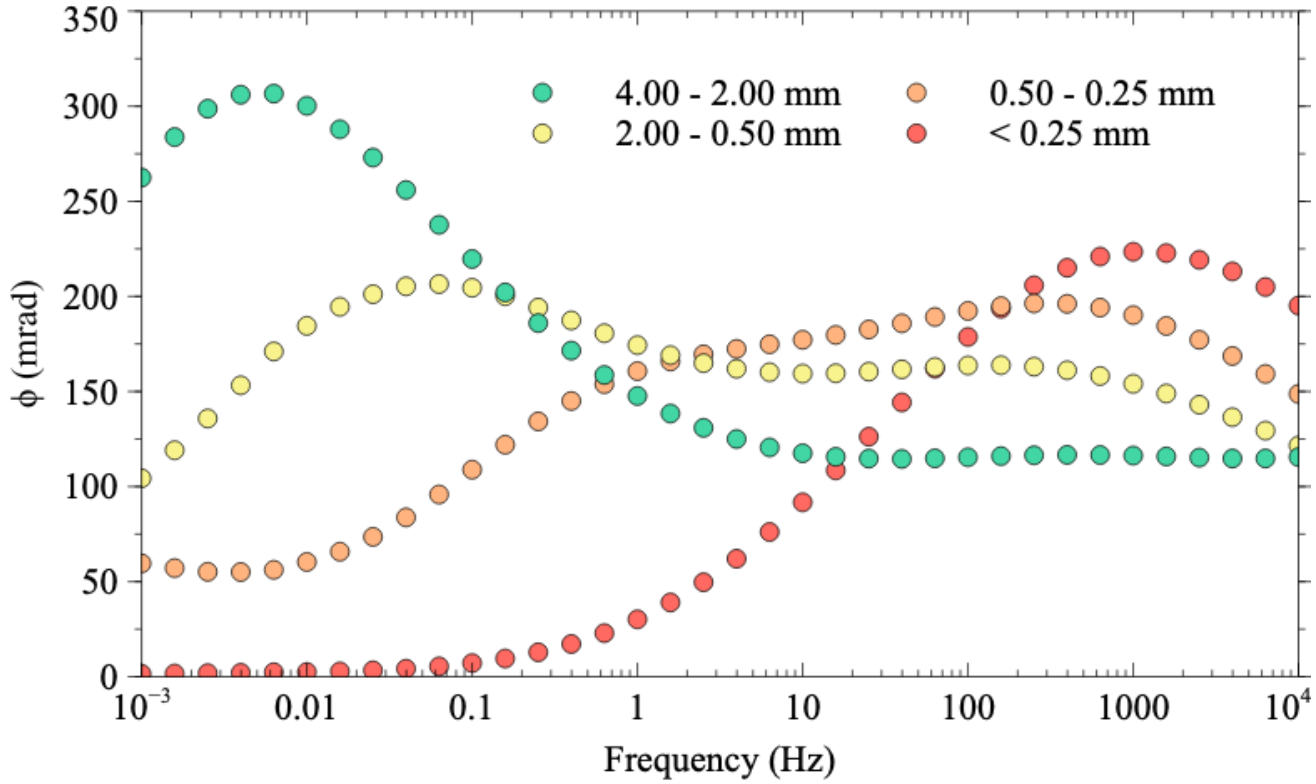
Grain size (BC7)



Experimental conditions

Solid (BW)	10`BC / 90 Sand %BW
Fluid (KCl)	300 uS/cm
Grain size	Sieved
	Duplicate measurements

- Grain size
  - Controls peak frequency
  - Impact on signal magnitude

SIP signatures of biochar!

- Each biochar appears to have unique SIP signature
  - SIP response is measurable (field)
- SSA and Carbon content appear not to be the main contributor to the SIP signals
  - Spor needs to be investigated

- SIP behavior very similar to graphite and metallic particles
  - Graphitization (graphite content in biochar) needs to be investigated

- Grain size impact needs to be investigated
  - Against SSA, Carbon content, Spor, Graphitization

- SIP should be considered for biochar characterization, and performance monitoring, in field applications
  - IP would be suitable in certain applications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