IDENTIFYING POLLUTANTS IN SOILS USING SPECTRAL INDUCED POLARIZATION

Idit Shefer, Nimrod Schwartz and Alex Furman

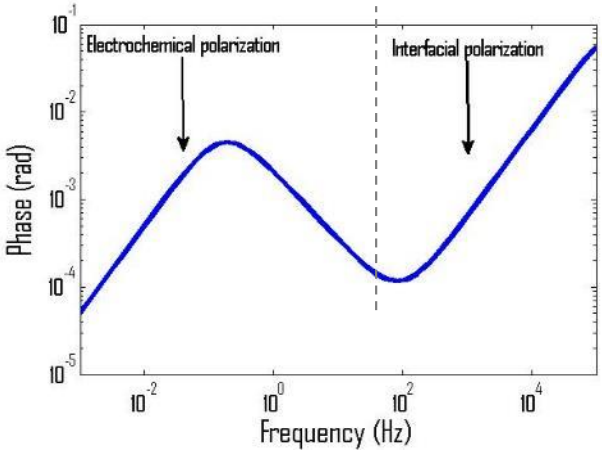
Outline

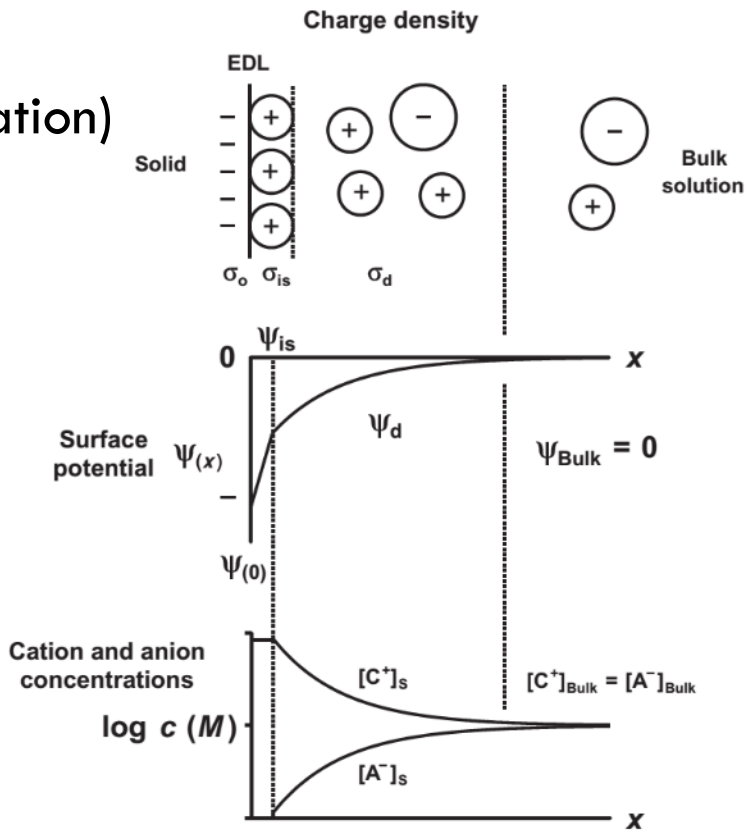
- IP Mechanisms
- Measurement system
- Research objectives
- The effect of organic contaminants on the electric signature
  - Free-phase
  - Various organic pollutants
- Using SIP as a tool to identify the soil's inorganic adsorbed phase and solution composition
- Preliminary predictive tool
- Summary and Conclusions

SIP mechanisms

Polarization of porous media indicated by the Imaginary part of complex conductivity σ“

- Electrochemical polarization (EDL polarization)
  - Stern layer polarization
  - Membrane Polarization
- Interfacial polarization (MW)

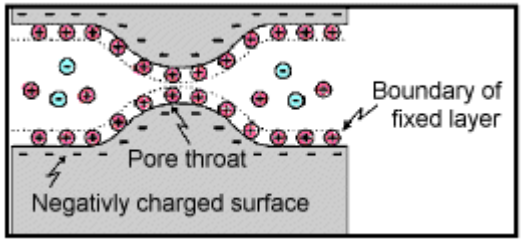


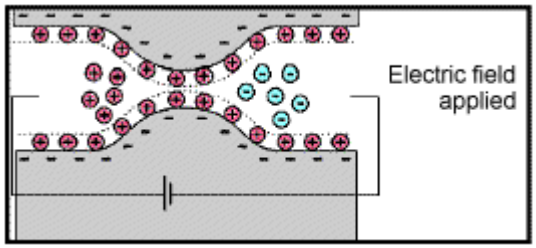


Membrane Polarization

Polarization of the diffuse layer and pore space. Concentration gradients and accumulation of charge in pore throats.

- Pore-throat scale
- Liquid arrangement
- Counter-ions composition
- No explicit consideration of surface chemistry





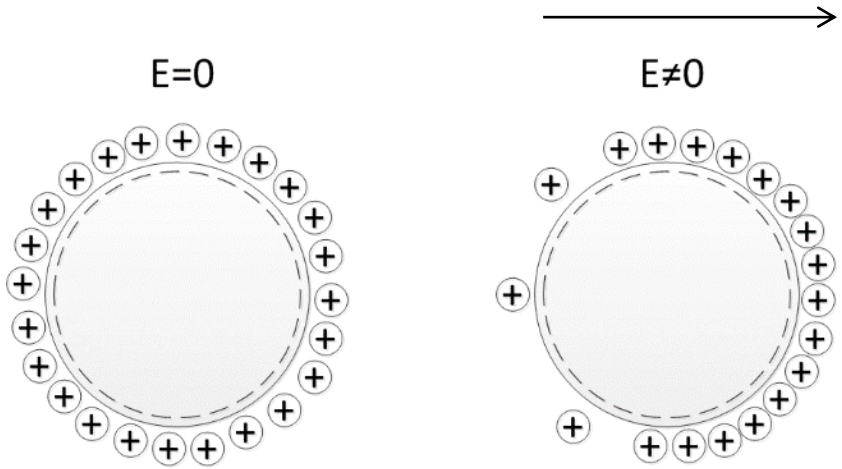
Stern layer polarization

Displacement of charge in the direction of the field.

- Tangential movement
- grain scale.
- Counter-ions composition and mobility

$$\tau = r^2 / 2D$$

$$\sigma^* = \frac{J}{E} = \frac{2\beta e \Gamma_0}{r}\left(\frac{i\omega\tau}{1 + i\omega\tau}\right)$$

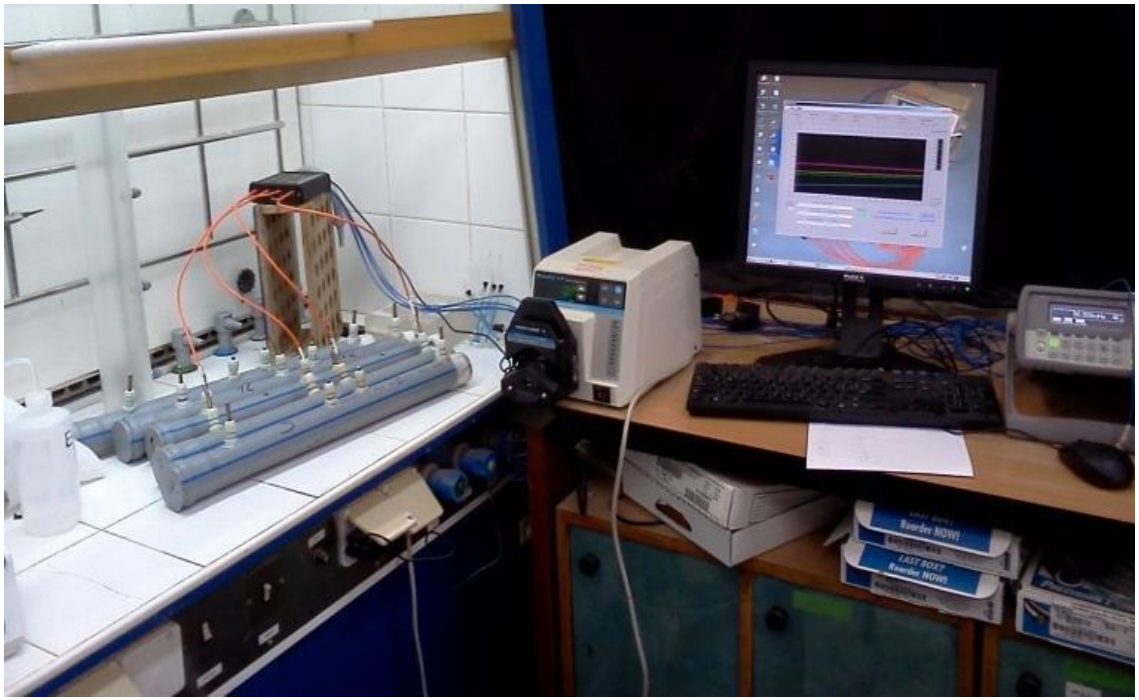


Measurement system

The SIP measurement system

ZEL-SIP04 Impedance spectrometer
(Forschungszentrum Julich) Germany

4 electrodes:
1mHz- 45KHz

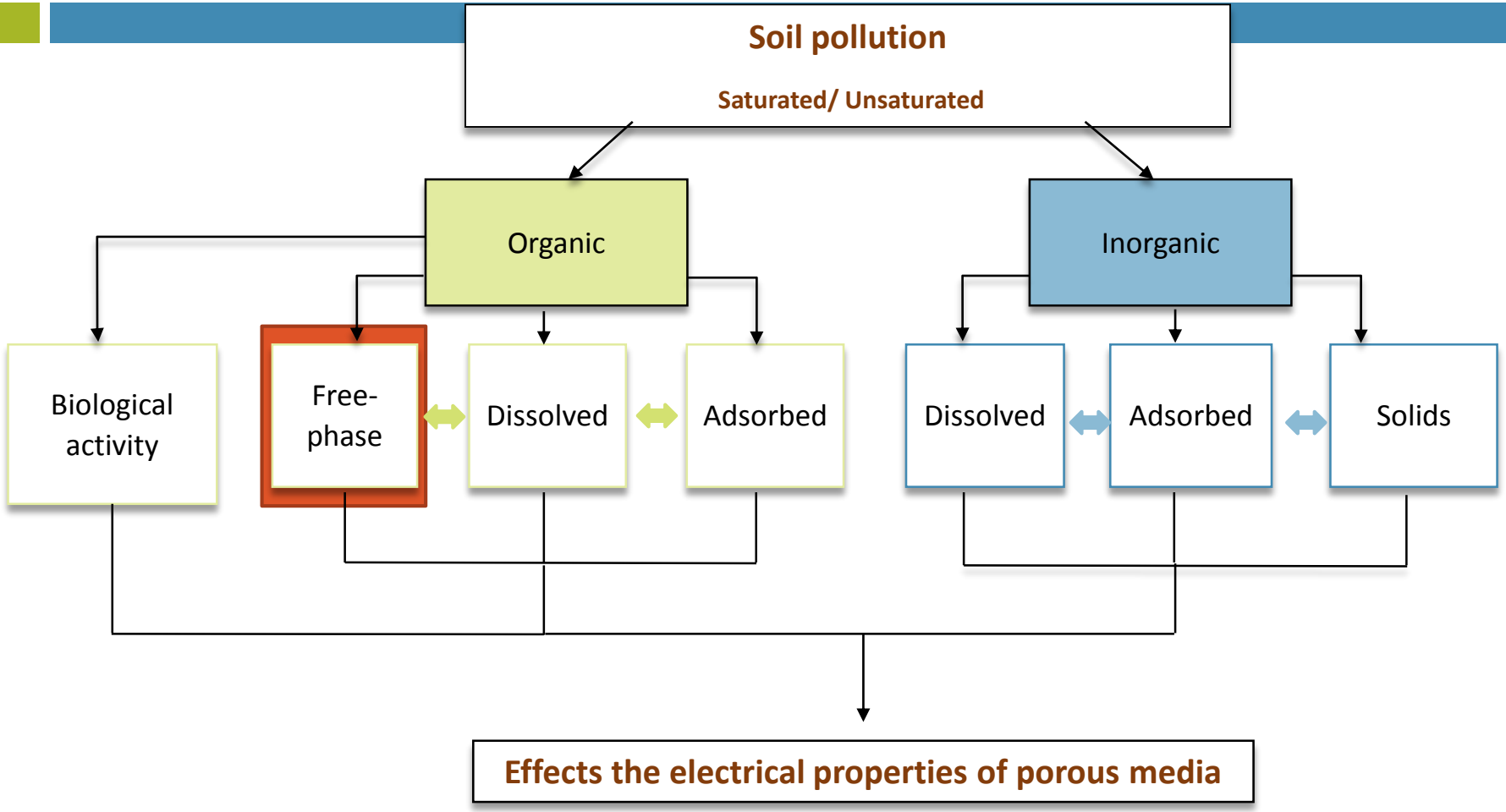


Zimmermann et al, (2008)

Objectives

- Examine SIP as a tool for identifying and quantifying the presence of pollutants in the soil

1) Examining how the presence of a free-phase organic contaminant (a fuel component) affects the SIP response of an unsaturated soil.
2) Investigate the effect of organic contaminants with varying properties (charged, polar, free-phase etc.)
3) Investigate the effect of various inorganic pollutants on the soil electrical signature


Soil pollution
Saturated/ Unsaturated
Organic
Inorganic
Biological activity
Free-phase
Dissolved
Adsorbed
Dissolved
Adsorbed
Solids
Effects the electrical properties of porous media

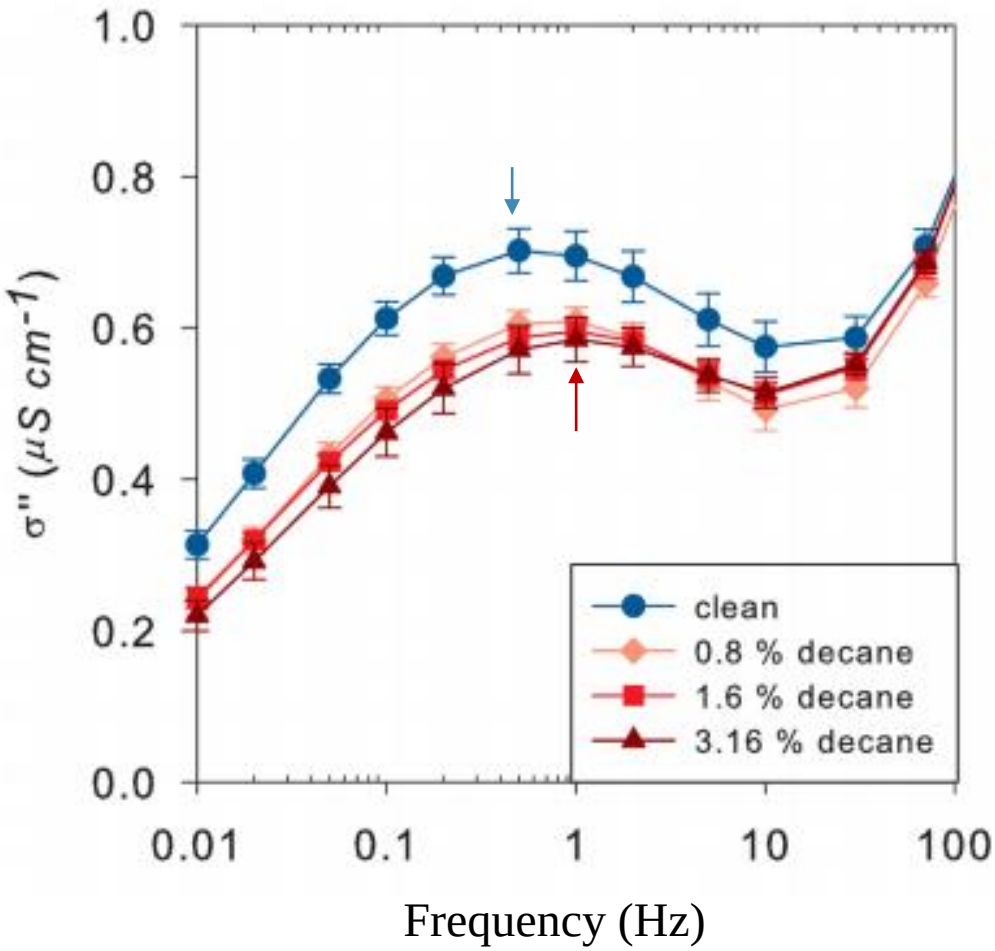
Free phase NAPL

- The soil's electrical response to organic pollutants is non-consistent.
- Different processes occur simultaneously with complex organics presence in a multi-phase porous media.

We examined unsaturated conditions with decane – negligible solubility in water.

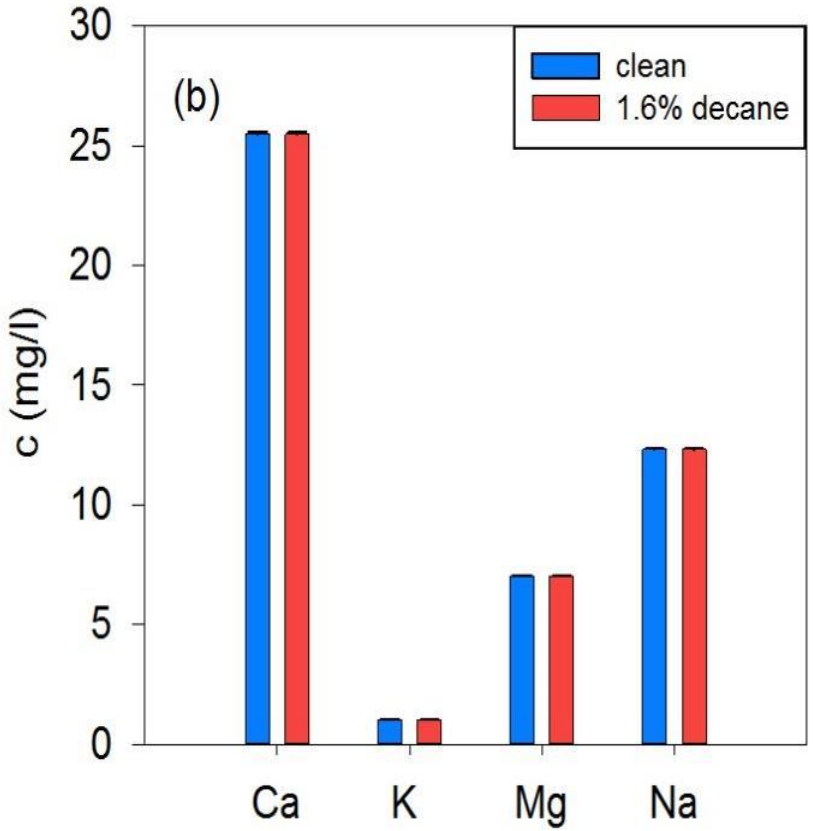
Results

- Addition of decane causes a decrease of polarization and relaxation time (i.e. increase of peak frequency)
- The amount of added decane doesn't change significantly the measured σ"
- No significant difference in the real part of the conductivity.

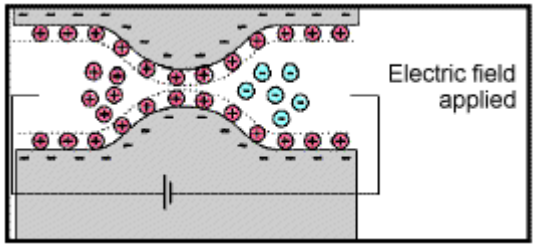


Shefer et al. (2013)

Results



- No evidence for changes in the surface chemistry
- Stern layer polarization cannot explain our results
- Membrane polarization- change in pore characteristic length



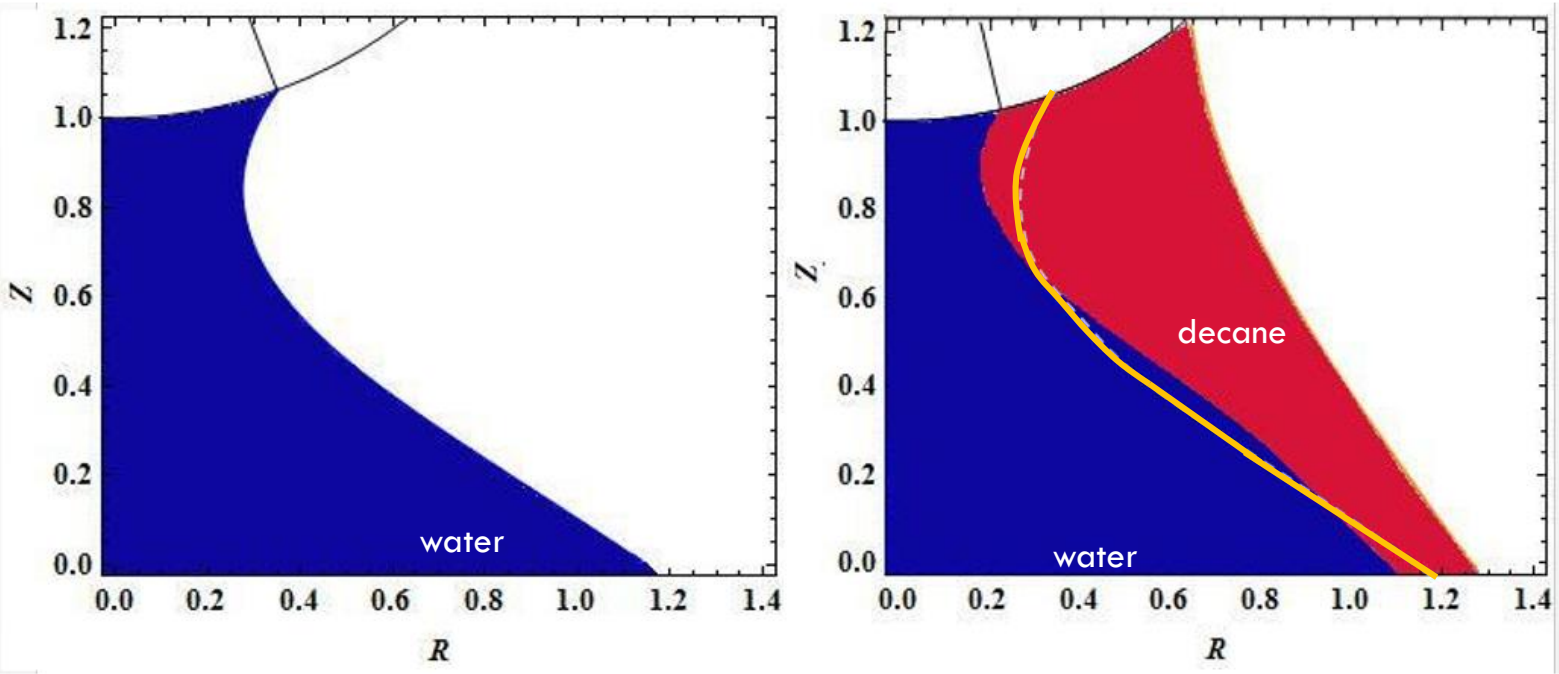
http://gpg.geosci.xyz/en/latest/index.html

Results

Changing geometry

Solution of Young-Laplace equation for decane-water in air.

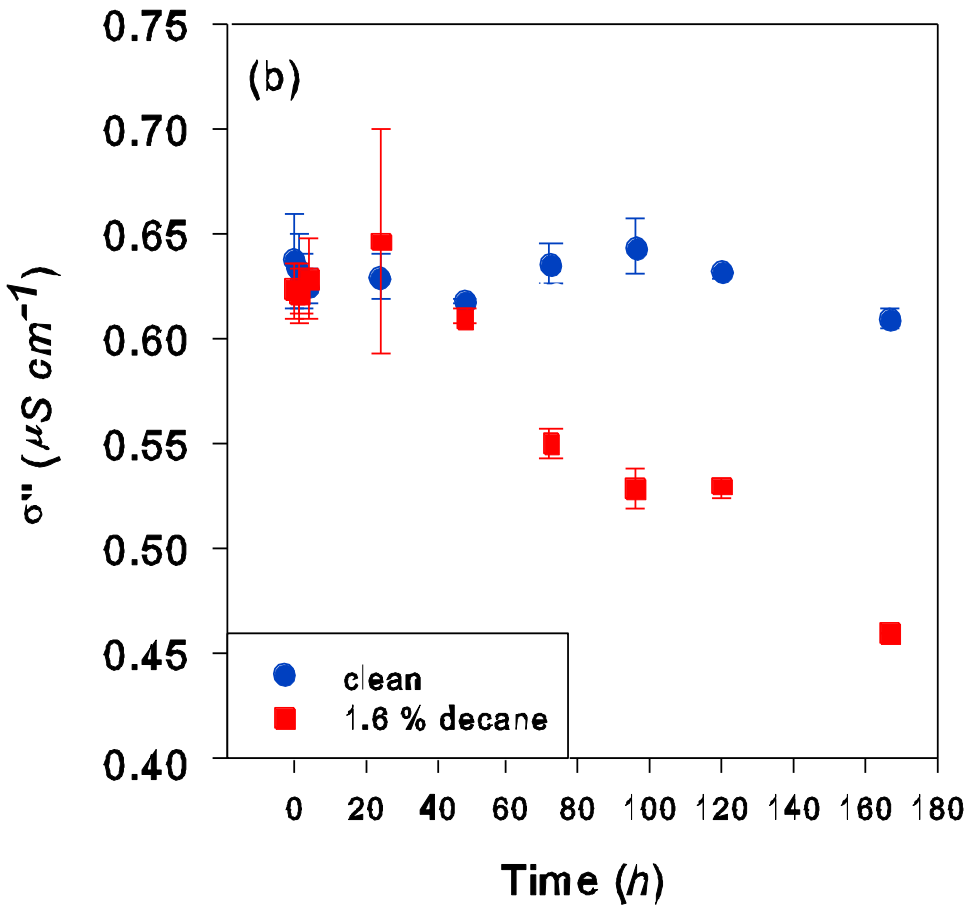
(courtesy of Leonid Fel)

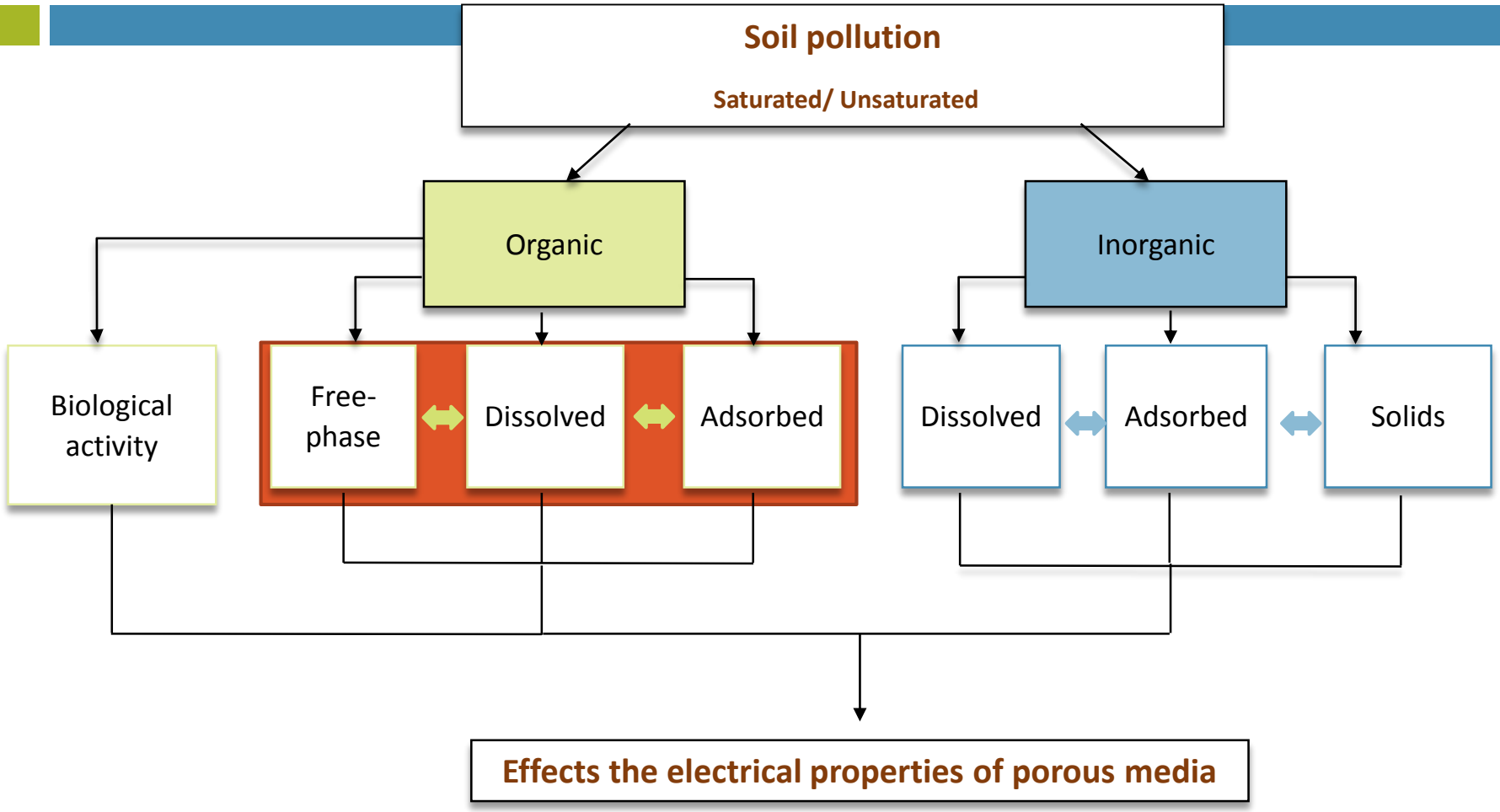


Results

Temporal changes

The polarization process is time related




Soil pollution
Saturated/ Unsaturated
Organic
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Free-phase
Dissolved
Adsorbed
Dissolved
Adsorbed
Solids
Effects the electrical properties of porous media

Various organic pollutants

- In reality many contaminated sites contain a mixture of different compounds
- Different organic compounds have different properties:

mechanism	organic functional group
cation exchange	amino, ring NH, heterocyclic N (aromatic ring)
cation bridging	carboxylate, amines, carbonyl, alcoholic OH
ligand exchange	carboxylate
water bridging	amino, carboxylate, carbonyl, alcoholic OH
anion exchange	carboxylate
hydrogen bonding	amino, carbonyl, carboxyl, phenolic OH
protonation	amino, heterocyclic N, carbonyl, carboxylate
van der Waals interaction	uncharged organic units

Underwood et al. (2015)

The goal of this study: distinguishing each pollutant unique influence on the soil's electrical signature for potential identification

Materials and Methods

- Loess soil (rich in calcium ions and $CaCO_3$ (6%))
- Decane containing vs. non decane containing treatments
- Packing in glass boxes and using sensitive NP electrodes.

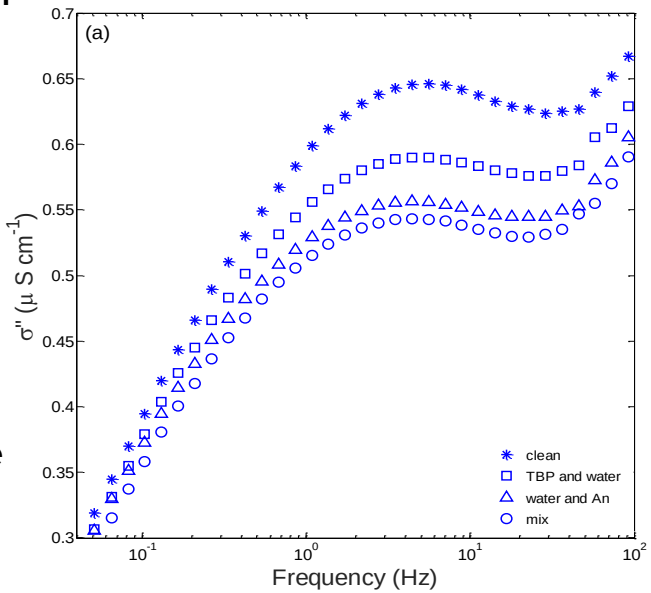
Non-polar | Polar/cation | Polar/anion | Cation

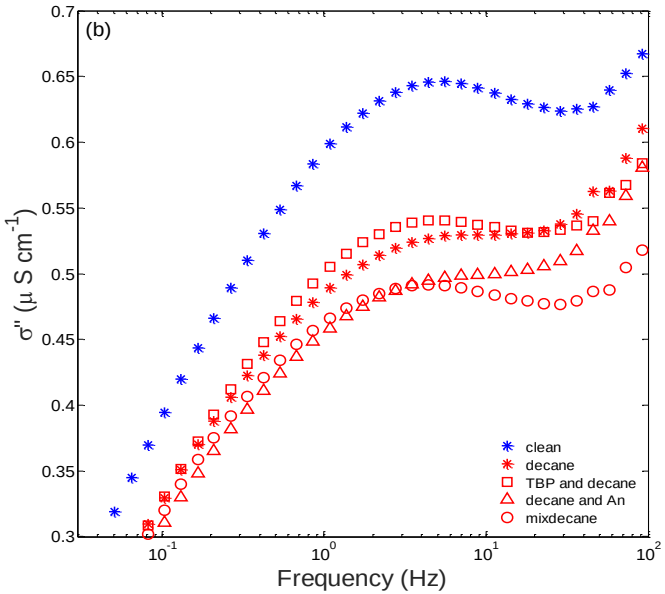
Treatment type		decane	aniline	TBP	HDTMAB
clean	0.01 N NaCl brine	-	-	-	-
aniline	0.13 mM Aniline in brine	-	+	-	-
TBP and water	0.13 mM TBP in brine	-	-	+	-
HDTAMB and water	0.13 mM HDTAMB in brine	-	-	-	+
mix	aniline and TBP in brine	-	+	+	-
decane	0.8 % decnae	+	-	-	-
TBP decane	2.7 mM TBP in decane	+	-	+	-
Andecane	2.7 mM Aniline in decane	+	+	-	-
Hdecane	0.143 ppm HDTMAB in decane	+	-	-	+
mixdecane	aniline and TBP in decane	+	+	+	-

Results

- Water treatments (non-decane) are distinguished from deacne containing in real part.

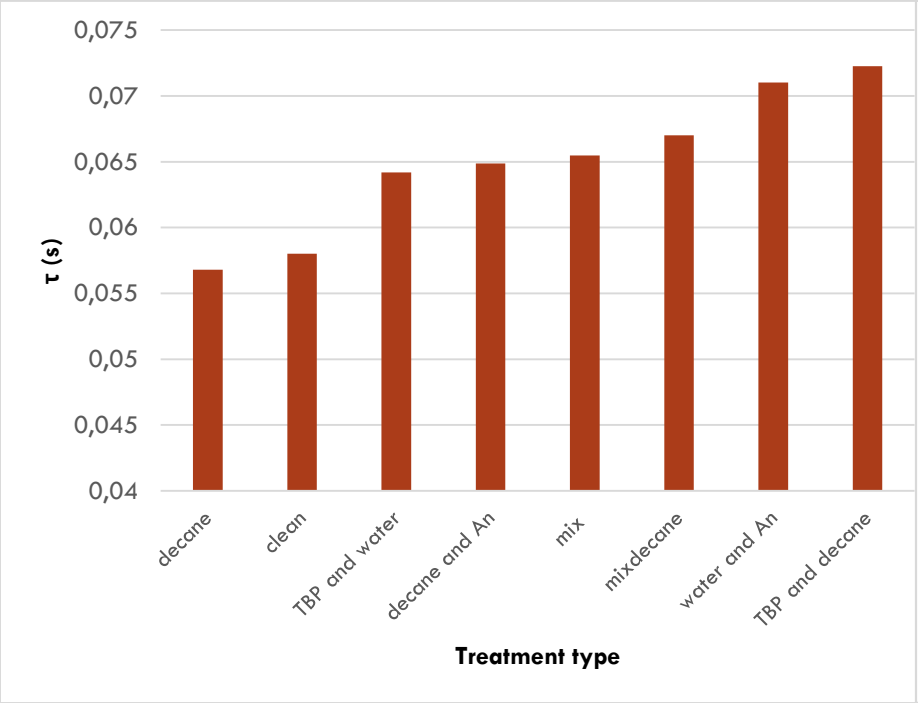
- complex reaction of imaginary part
- Decrease with decane addition
- Aniline suppresses polarization stronger than TBP
- Shifts in relaxation time

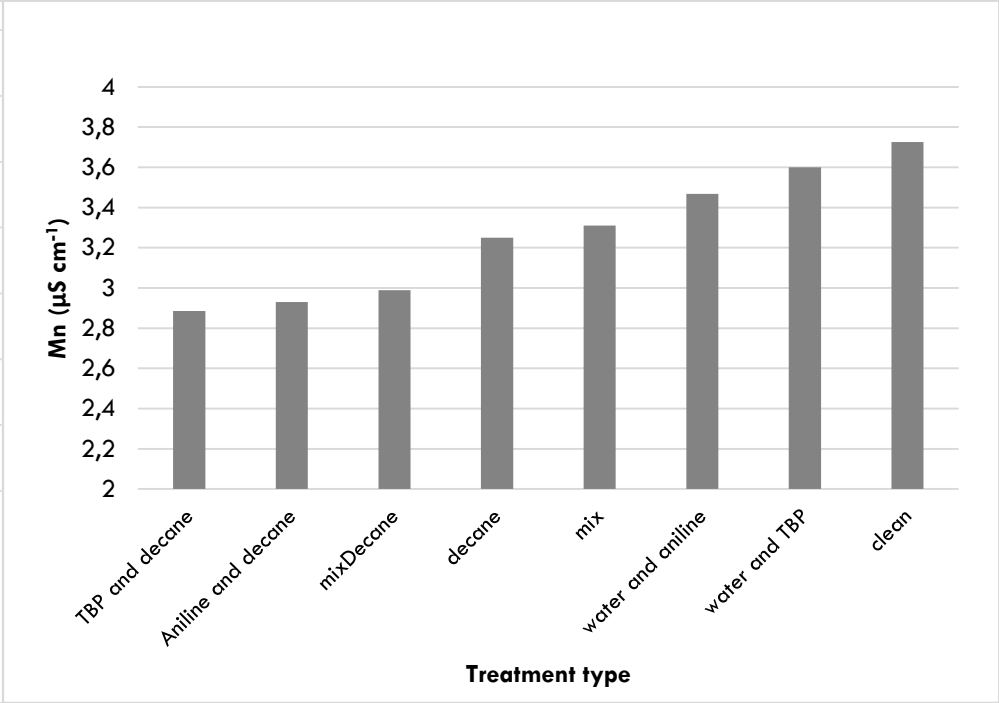




HDTMAB results are not presented due to technical problems in electric and chemical measurements

Results



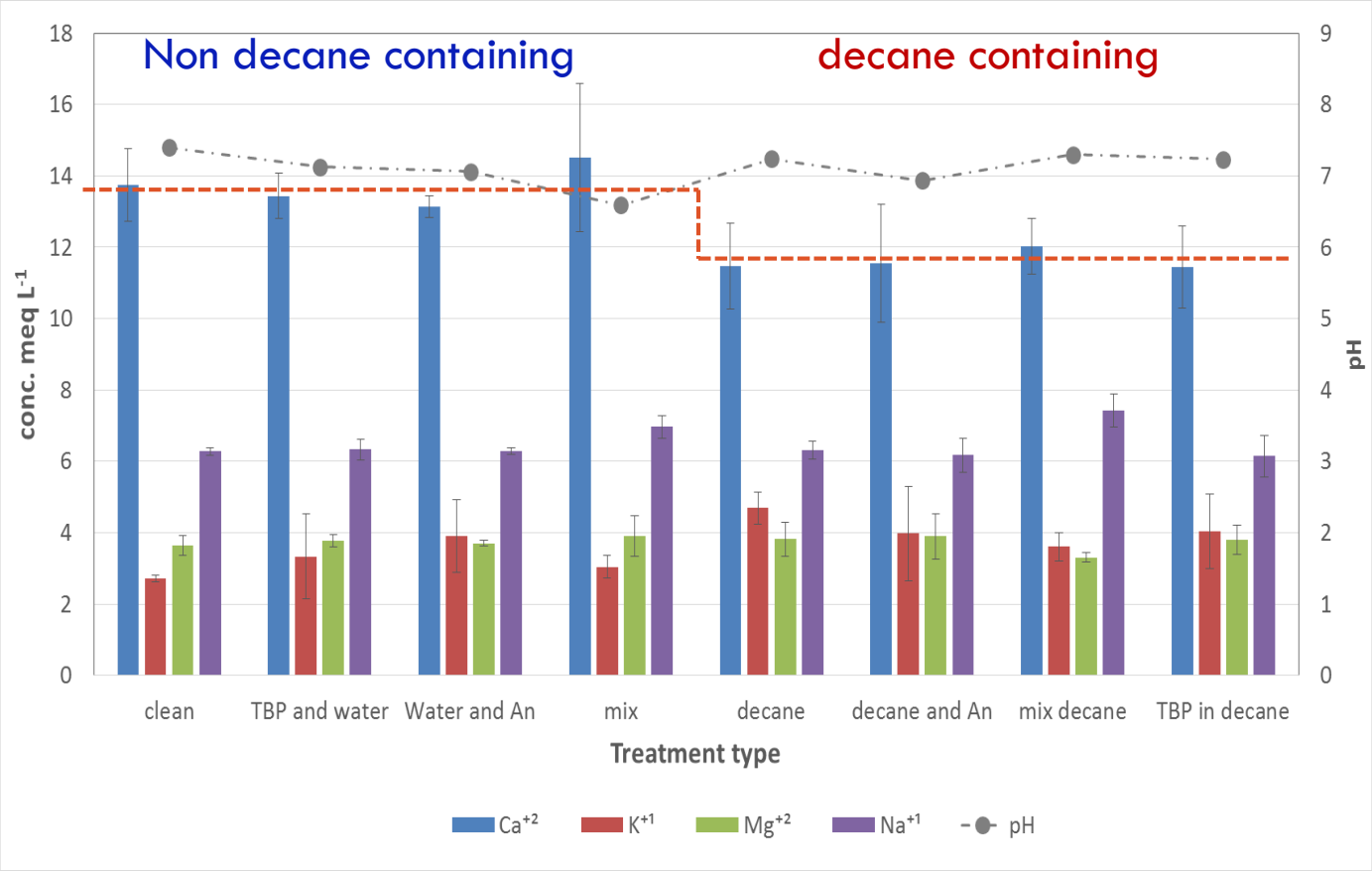


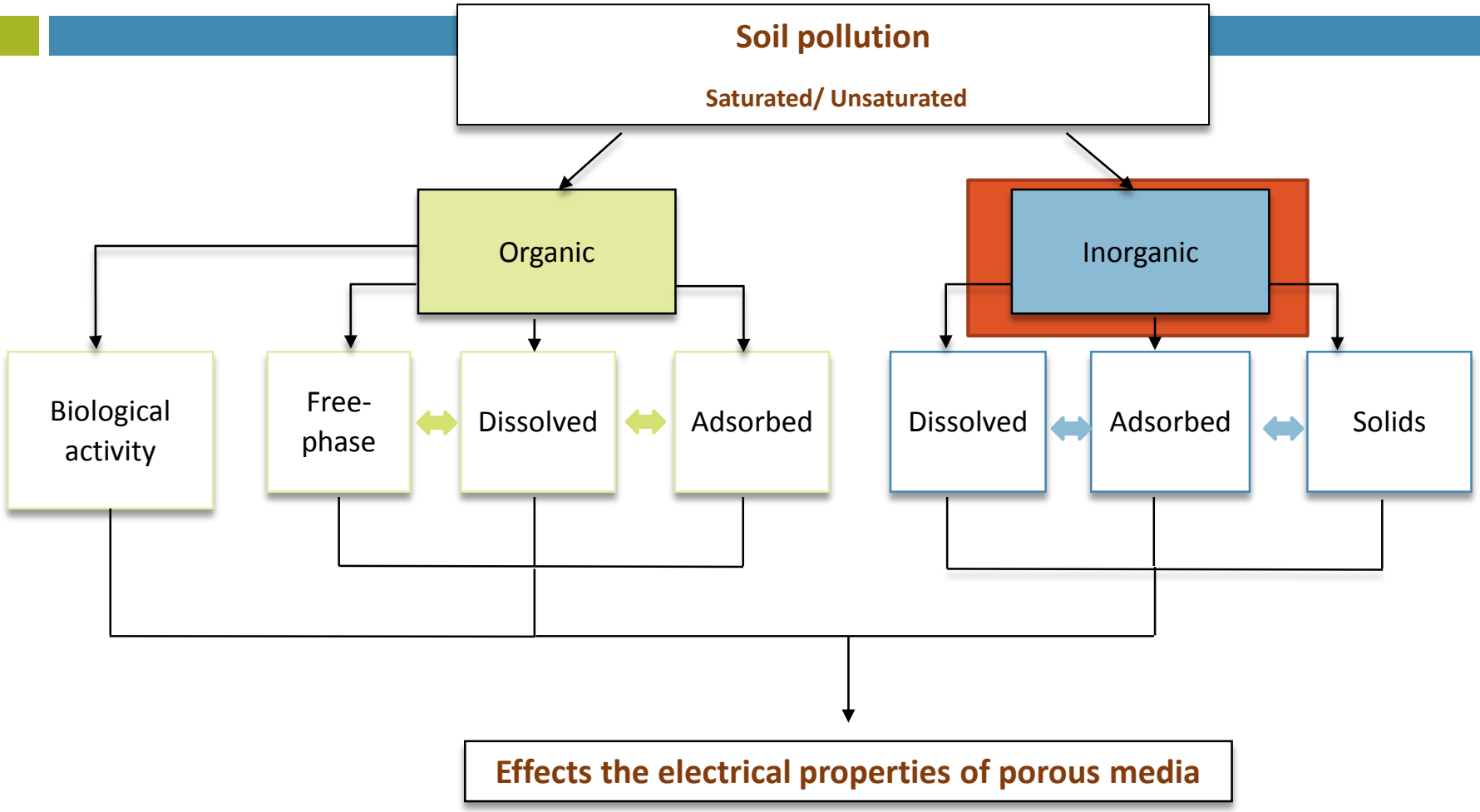
- Cole-Cole relaxation time constants: lowest for decane and highest for TBP in decane
- Decane containing treatment chargeability is lower than the clean treatments
- The presence of other organic compounds changes the way decane influences the polarization and relaxation time

$$\sigma^*_{CC}(\omega) = \sigma_0 \left[\sum_{l=1}^{L} \frac{1}{1-M_l} \left(1 - \frac{M_l}{1+(i\omega\tau_l)^{c_l}} \right) \right]$$

Results

- Ca^{+2} concentrations ions are lower in solution extracts of decane containing treatments
- No dramatic changes in pH (7±0.4)

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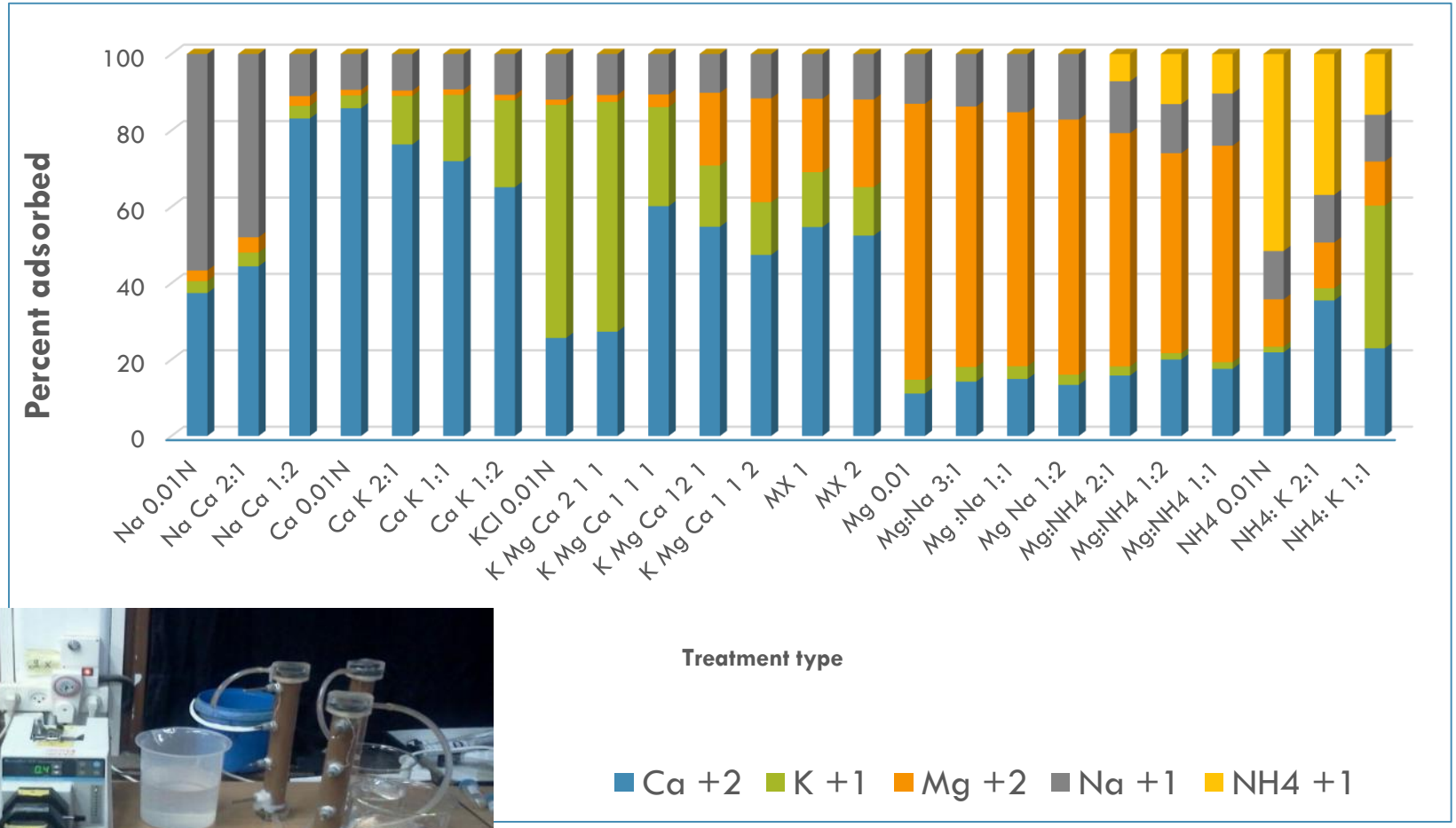
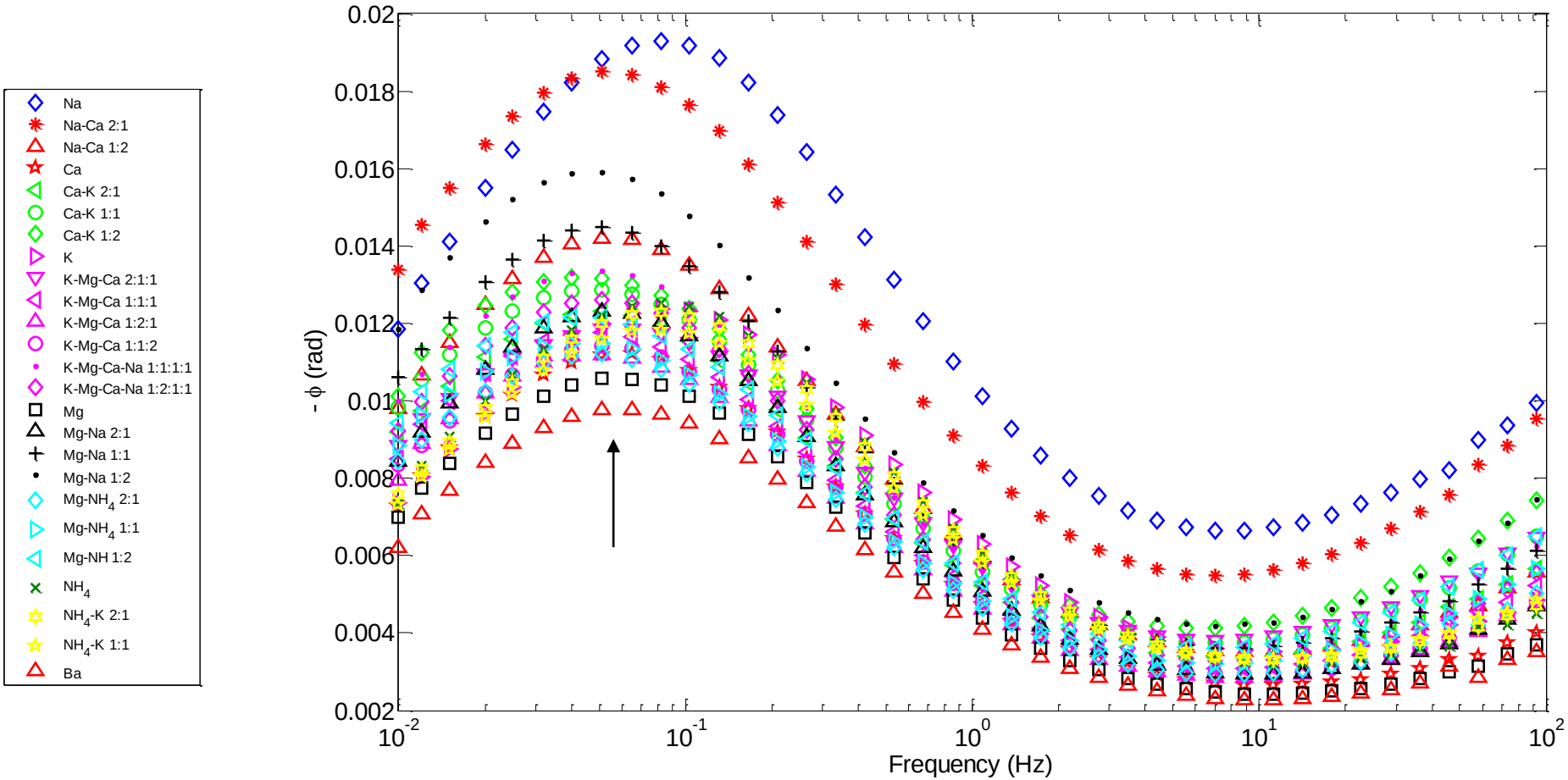
Material and Methods

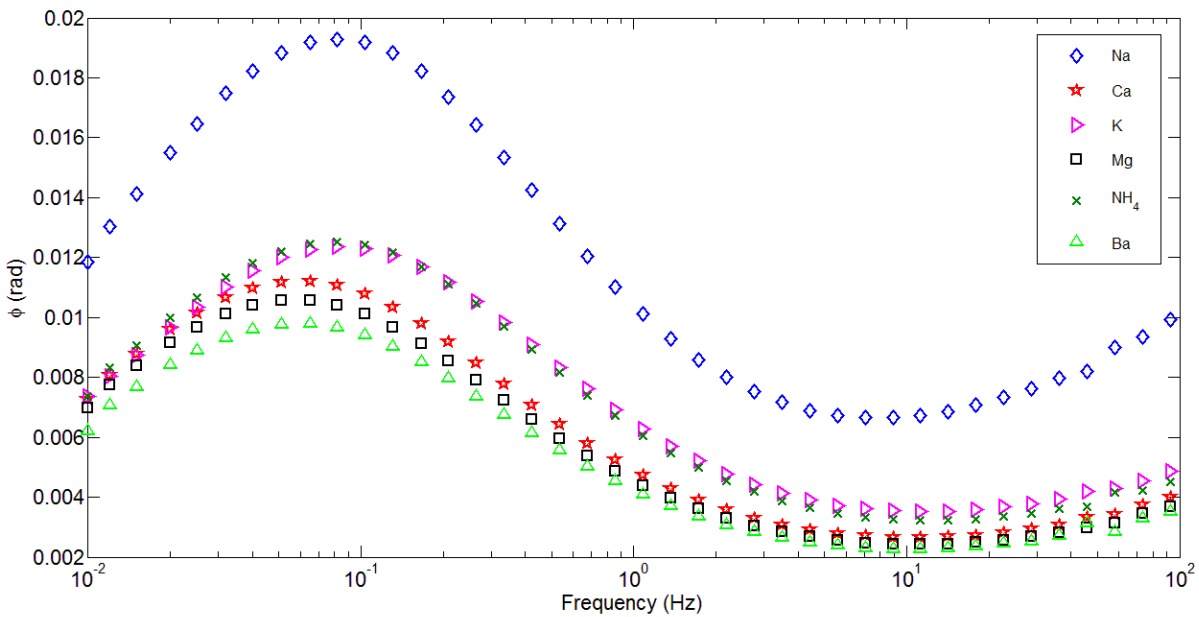


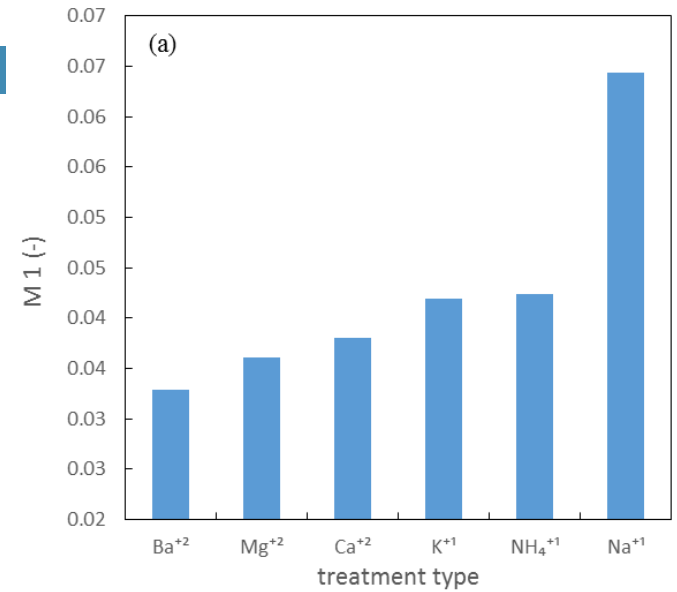
Results- spectra for all treatments

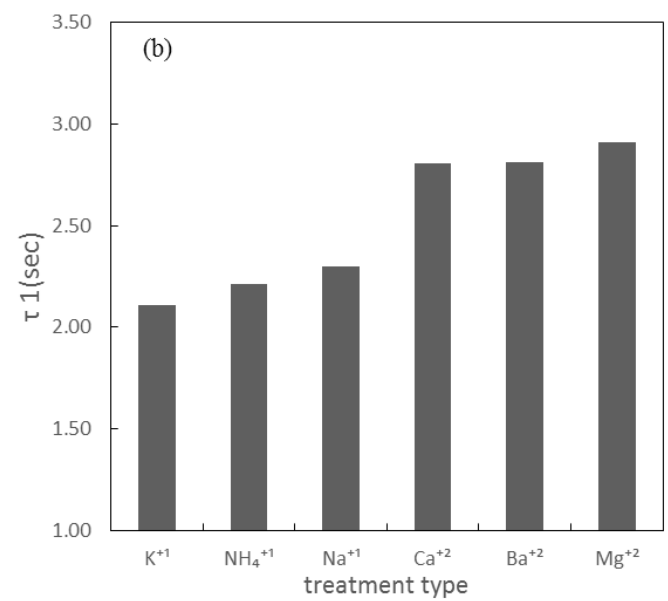


Changes in phase value (polarization) and shifts of relaxation times

Major cations



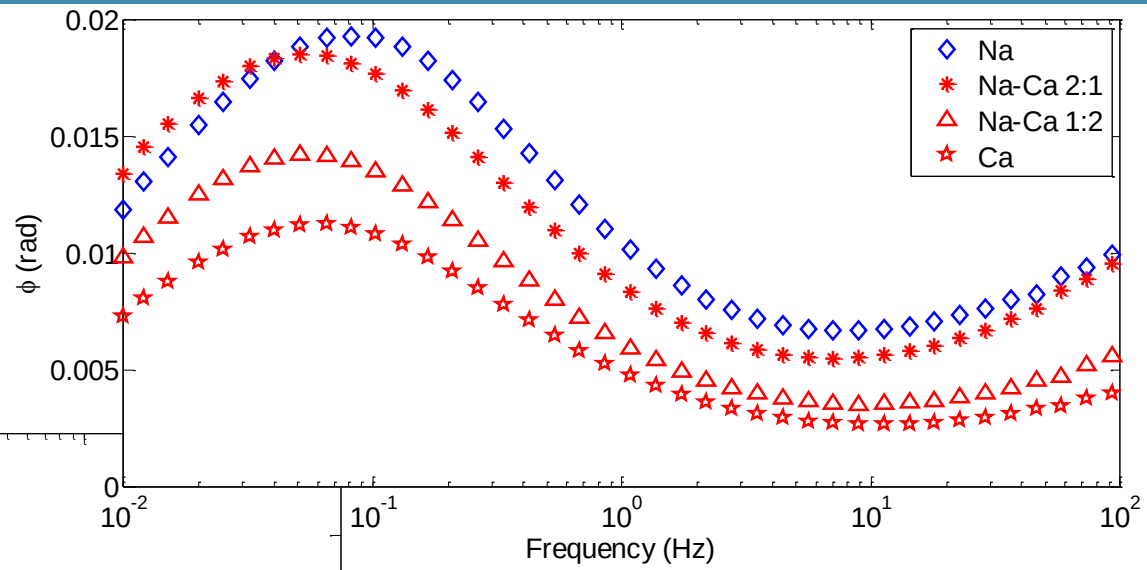


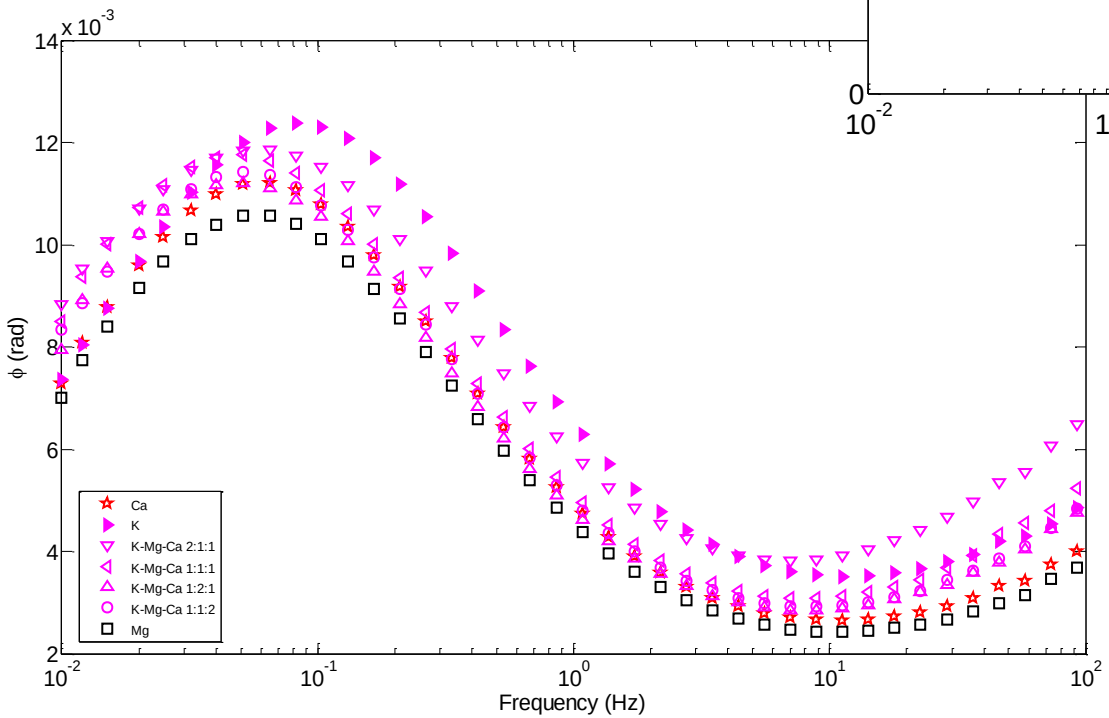


Clear distinction between mono and divalent cations.

Different combinations

Changes in solution composition changes relaxation frequency and polarization magnitude





	T (s)
Na	2.29
Na-Ca 2:1	3.29
Na:Ca 1:2	3.11
Ca	2.81
K	2.11
Mg	2.91
K-Mg-Ca 2:1:1	3.15
K-Mg-Ca 1:1:2	3.28

Simplified chemical model

Surface complex conductivity

$$\sigma_s^* = \frac{2}{r_0}\left(\Sigma_d + \sum_i \left(1 - \frac{1}{1+(i\omega\tau_{0i})^{c_i}}\right) e\beta_i |z_i| \Gamma_i\right)$$

β ??

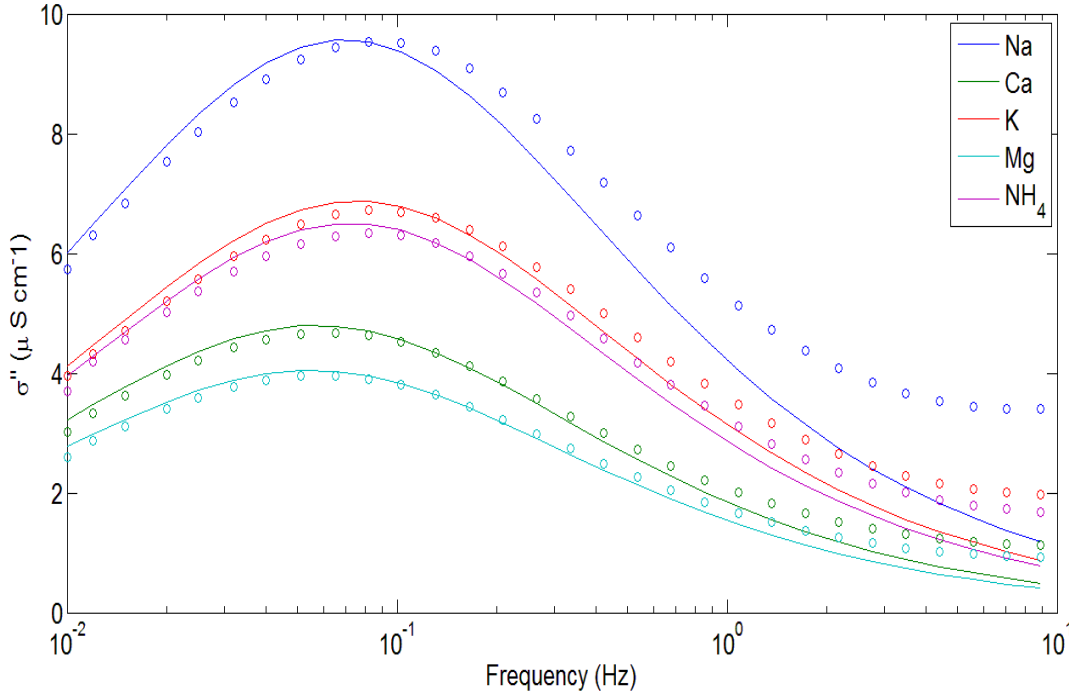
From Revil and Florsch (2010)

Optimization for finding the ions cations mobilities

Γ_i Surface site density of specie i- the adsorbed percentage of the total surface site density.

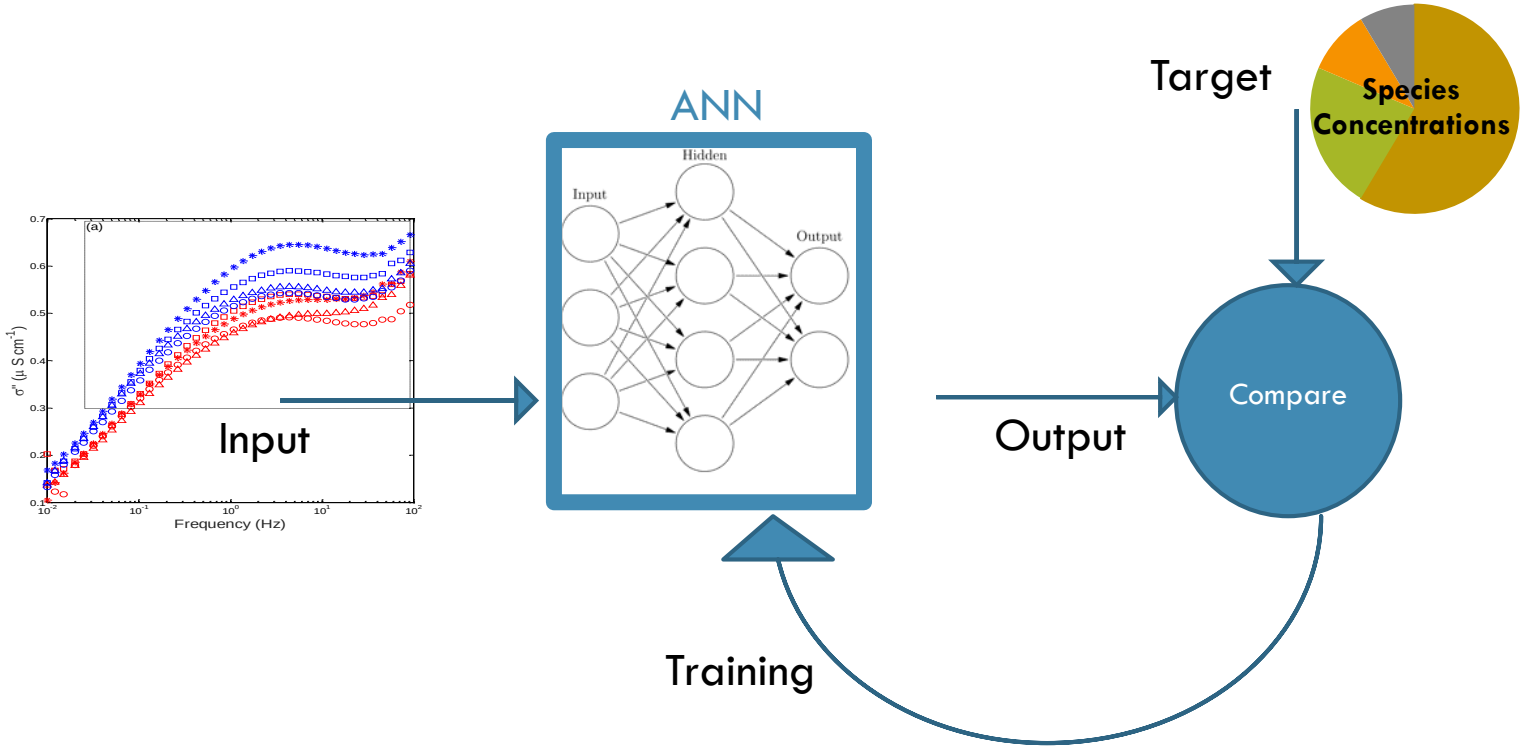
τ , C from fitted data.

Simplified chemical model

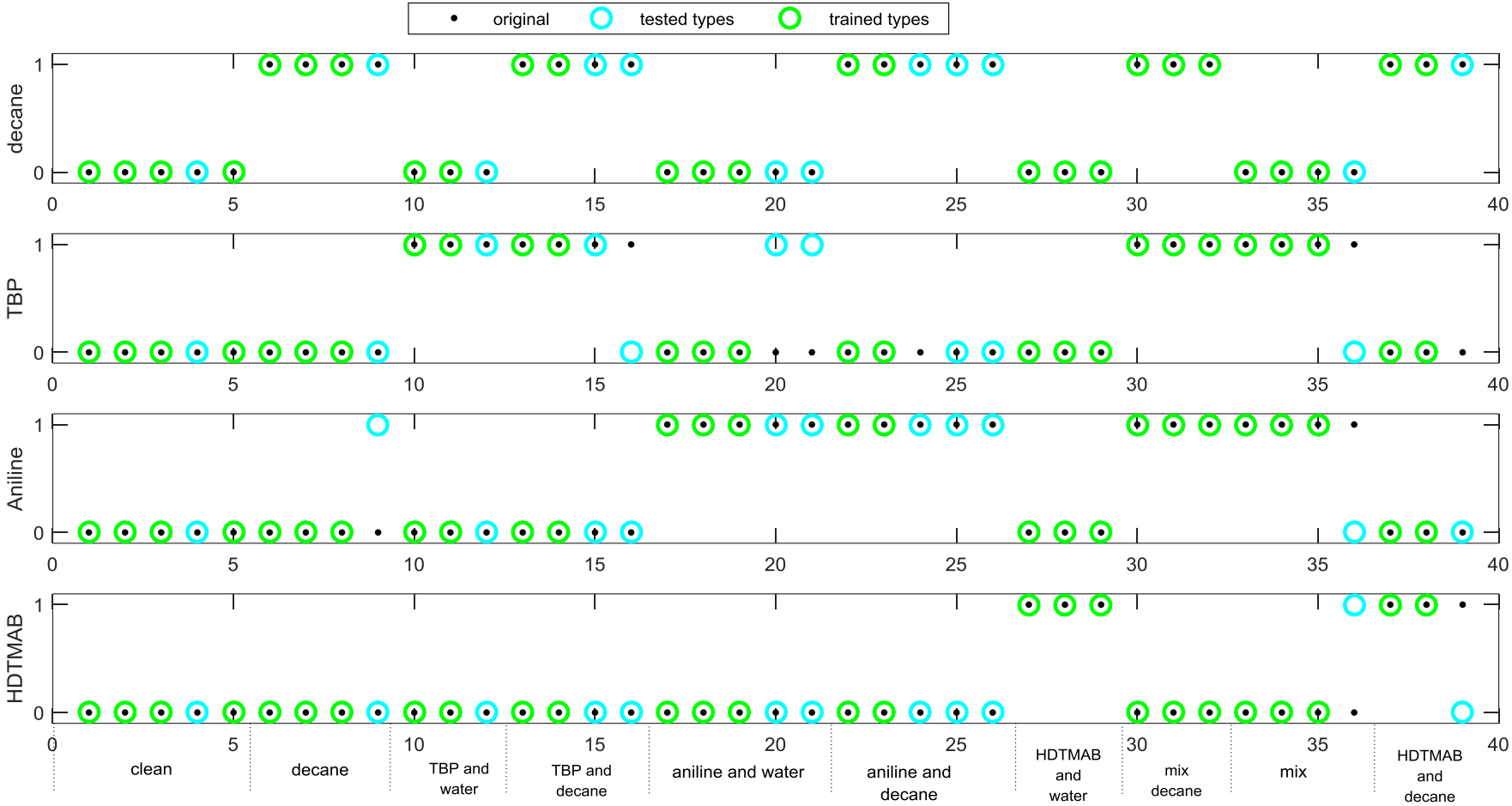


Cation	Ca^{+2}	K^{+1}	Mg^{+2}	Na^{+1}	NH_4^{+1}
Mobility (10^{-9} m^2 s^{-1} V^{-1})	7.27	24.29	1.87	82.2 **	20.79

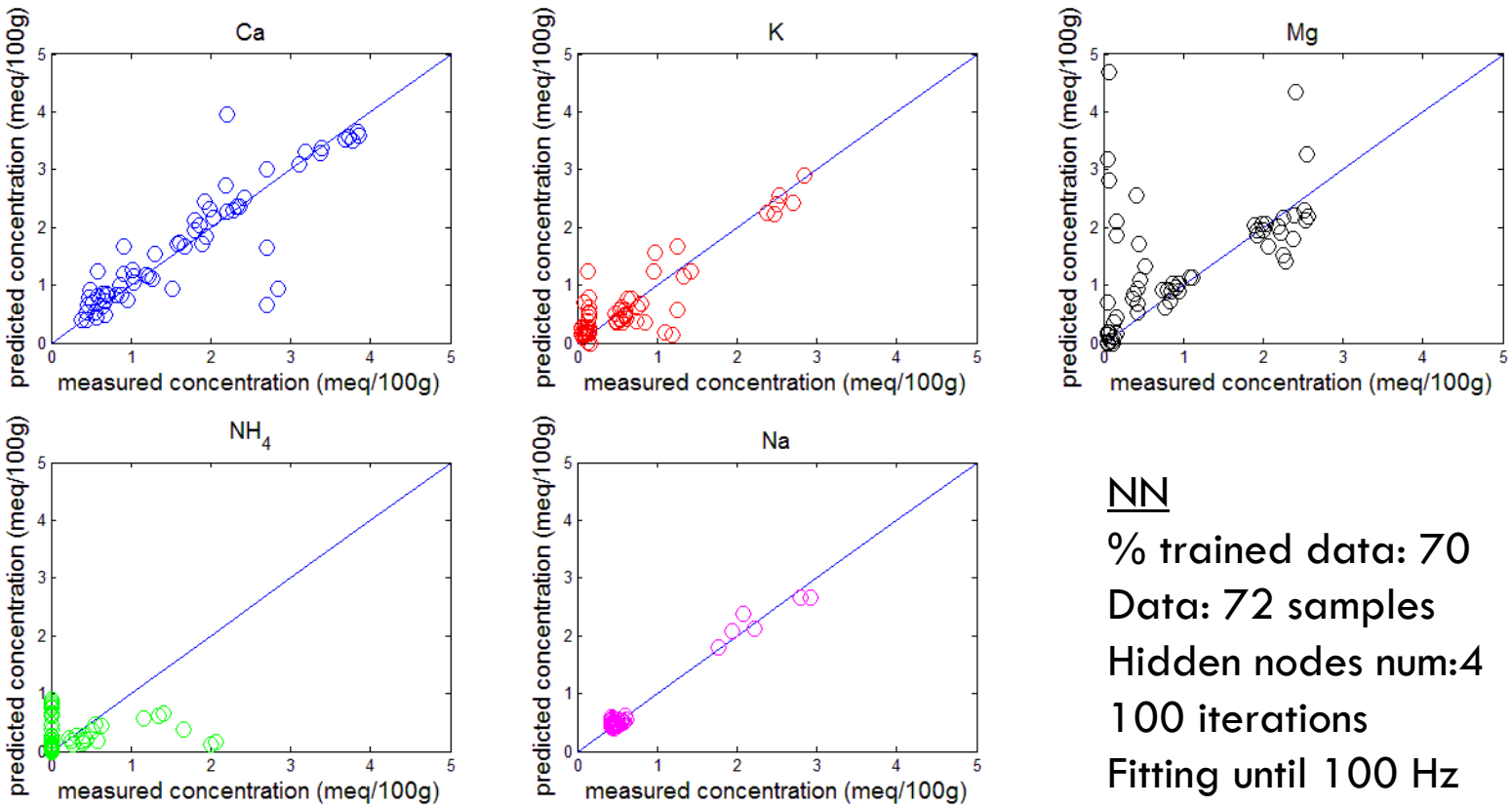
Artificial Neural Network



Preliminary neural network classification of organic pollutants presence



Preliminary ANN inorganic species concentration prediction



NN

% trained data: 70

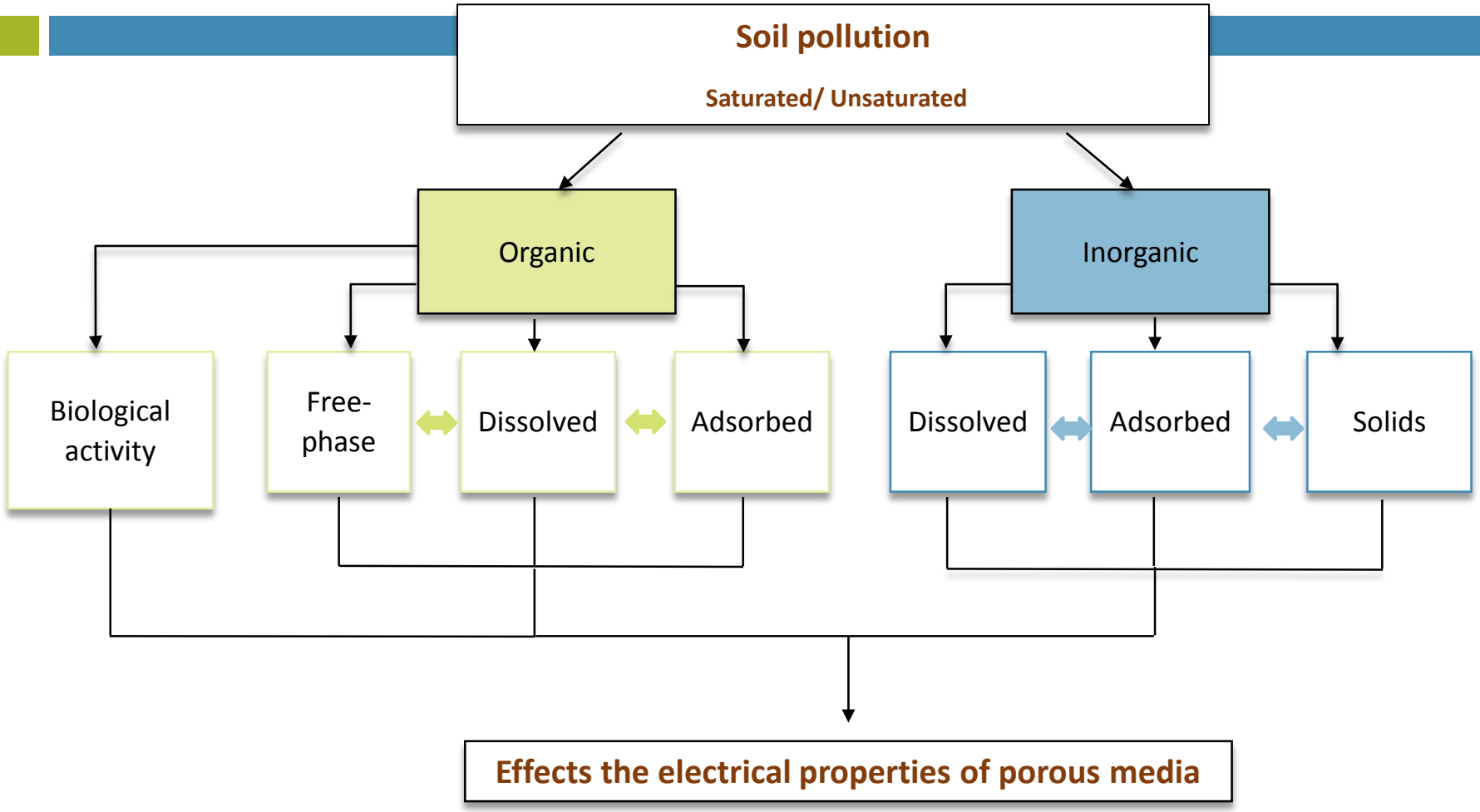
Data: 72 samples

Hidden nodes num:4

100 iterations

Fitting until 100 Hz

* Difficulty at lower concentrations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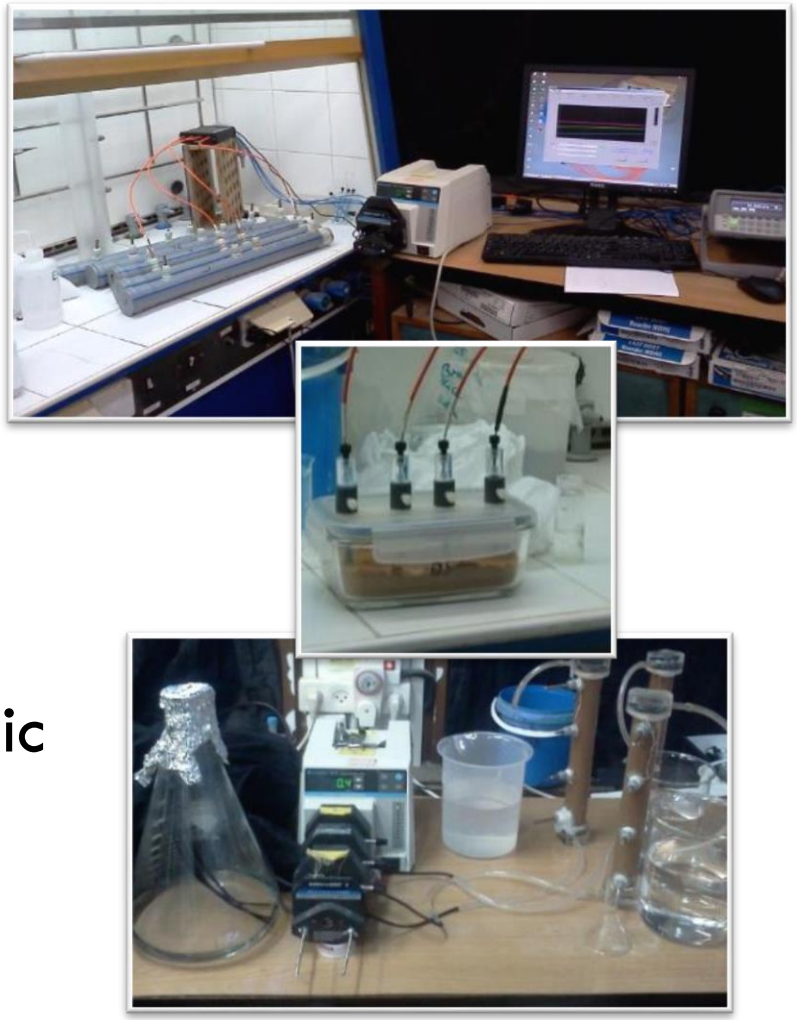
Summary

- Examined how a free-phase organic contaminant (decane-a fuel component) affects the SIP response of an unsaturated soil.
- The effect of various organic contaminants with varying properties (charged, polar, free-phase etc.)
- Investigated the effect of inorganic species on the soil electrical signature



Conclusions

- Membrane polarization model is the dominant mechanism to explain the findings of free-phase contaminant: time related liquid arrangement.
- Calcium cations play important role in surface interactions with soil mineral and OM in the presence of hydrocarbons (membrane & stern layer polarization)
- The properties (mobility, valence, radii, affinity) of the adsorbed cations affect the electrical signature of the soil: changes in polarization and relaxation time
- The measured spectra has the potential to reveal adsorbed concentrations or classify the presence of dominant species at the solid surface.
- The exact surface interactions are yet to be fully understood

Thanks for listening!

Future work

- Increasing database
- Improving models for classification and identification
- Medium and field scale measurements
- Further investigating mechanisms and factors dominating the electrical signature of various soils and pollutants, i.e. deeper understaffing of surface interactions

Acknowledgments

- Alex!
- Former group (Nimrod, Ziv) and current (Hana, Elazar, Tal) members
- Lab assistants: Goory, Maya, Tamar
- Leonid Fel
- Malik, Sara, Utah
- My family and pets

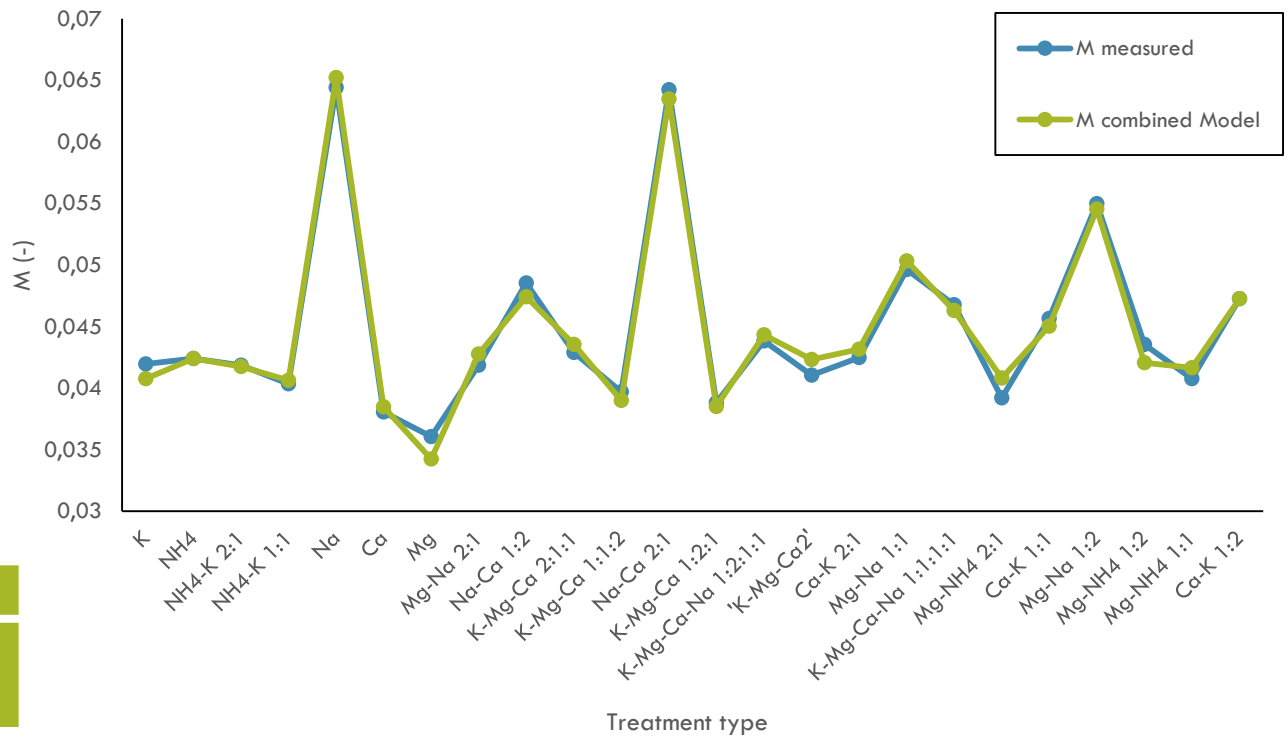
Simple regression model

Combination of both adsorbed and solution concentrations -for all the data

$$M_{treatment}=a_1\cdot[Ca]+a_2\cdot[K]+a_3\cdot[Mg]+a_4\cdot[Na]+a_5\cdot[NH_4]$$
$$+b\cdot T+c_1\cdot\{Ca\}+c_2\cdot\{K\}+c_3\cdot\{Mg\}+c_4\cdot\{Na\}+c_5\cdot\{NH_4\}$$

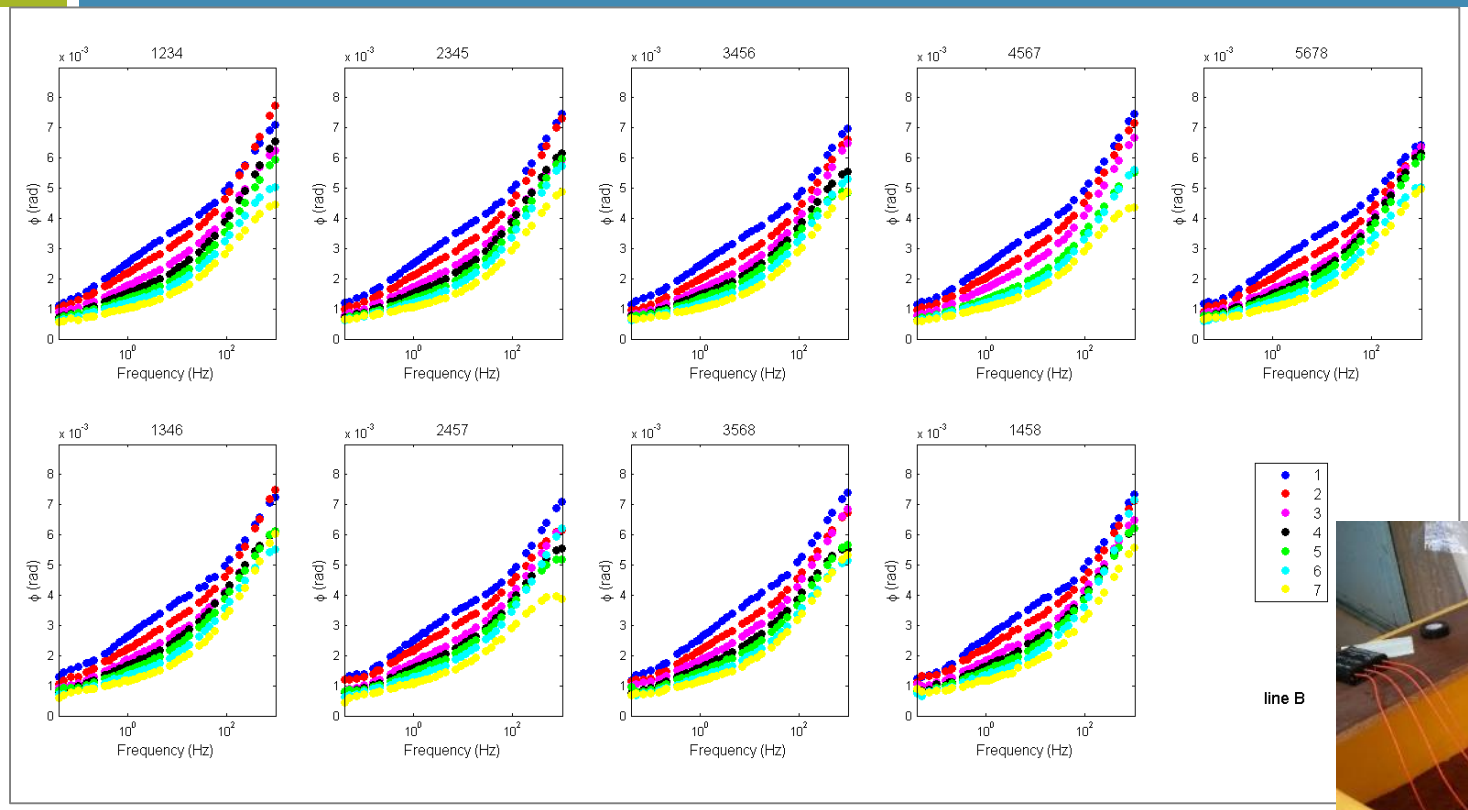
$a_{1\text{-}5}$ coefficients for solution concentrations

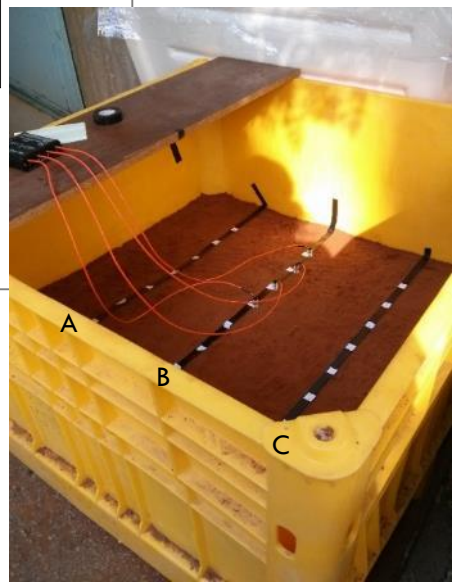
$c_{1\text{-}5}$ coefficients for adsorbed concentrations.



RMSE	7.4 e-4
Relative RMSE	1.7 e-2

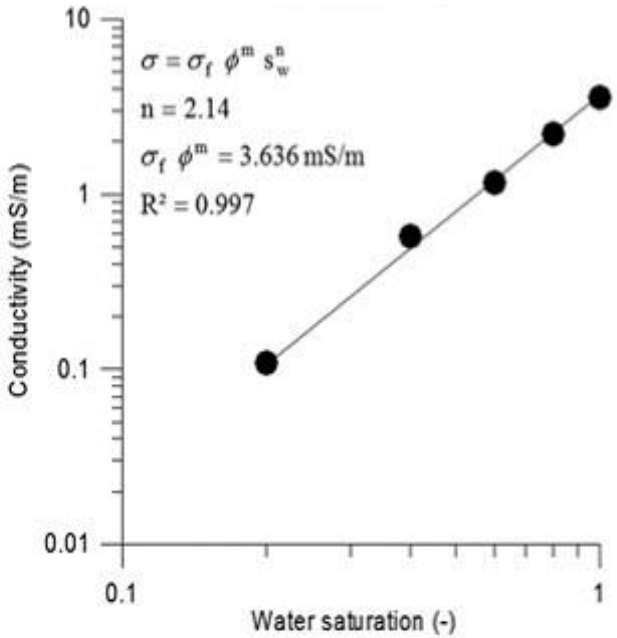
General summary and Future work



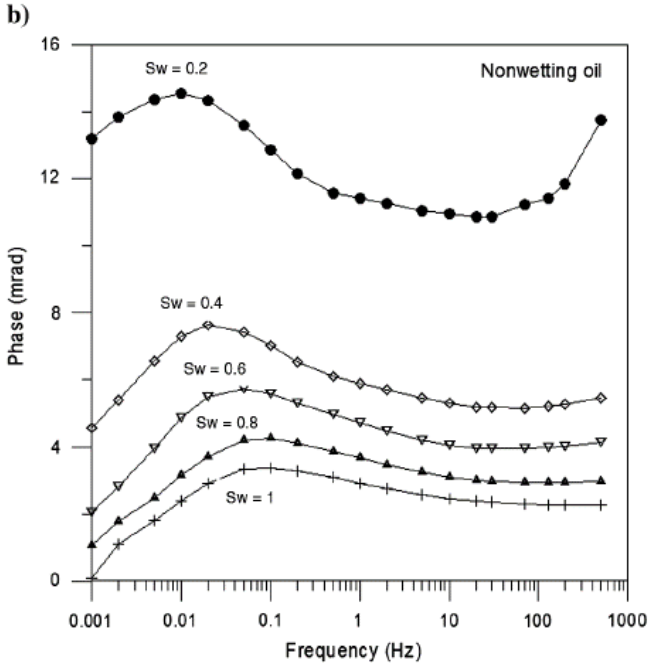


Previous works

- Most previous works- saturated media.
- The soil's electrical response was mainly influenced by the change in the bulk electrical conductivity- water saturation vs. NAPL (non aqueous phase liquid) saturation



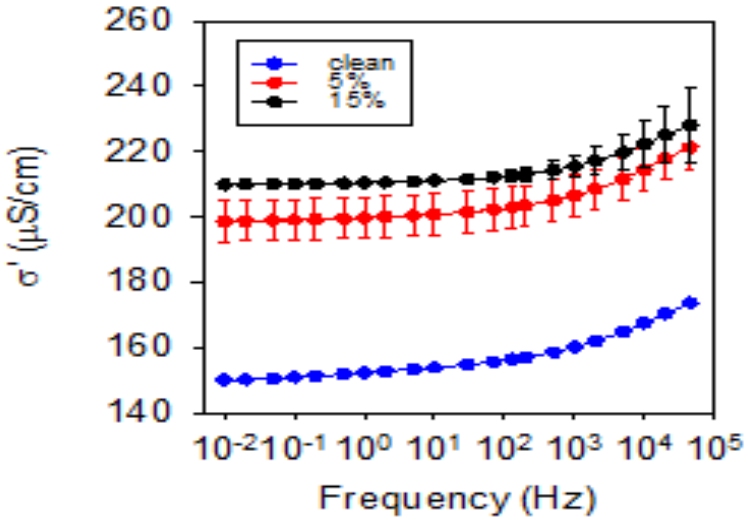
Schmutz et al (2010)



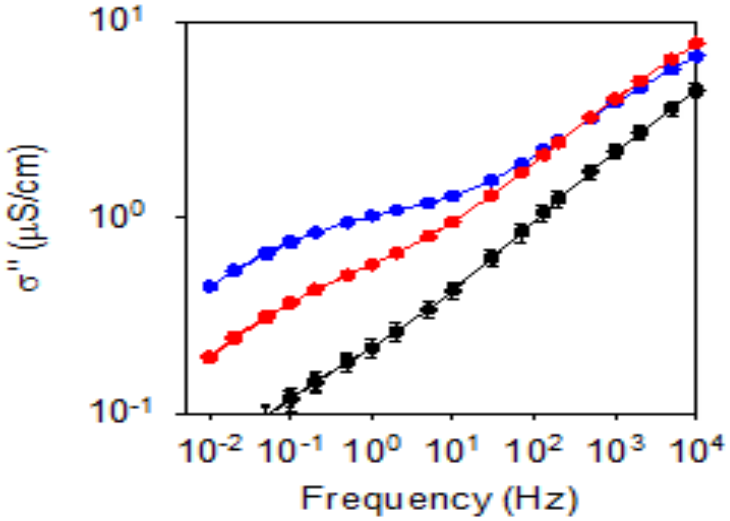
revil et al (2011)

Previous works

- SIP signature of complex organic compounds. Addition of diesel and/or motor oil causes a decrease in the imaginary part of the complex conductivity and increases the real part – exchange processes (Schwartz et al., 2012)



- Addition of cationic organic compound to the soil causes a decrease in polarization due to low mobility of the adsorbed organic compound (Schwartz and Furman, 2012)



Mathematical model

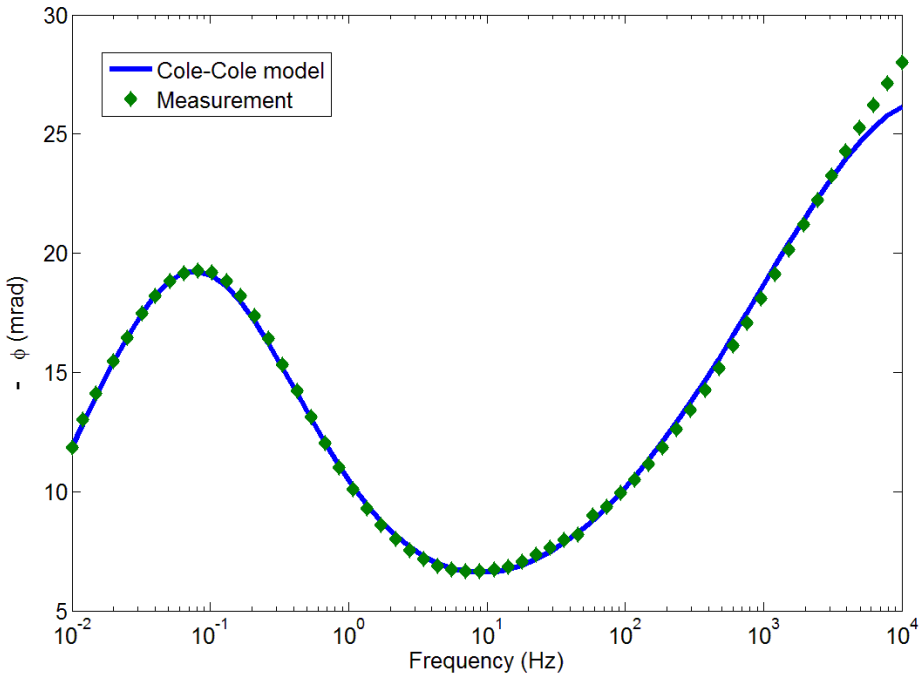
Cole-Cole model:

$$\sigma^*_{CC}(\omega) = \sigma_0 \left[\sum_{l=1}^{L} \frac{1}{1-M_l} \left(1 - \frac{M_l}{1+(i\omega\tau_l)^{c_l}} \right) \right]$$

M chargeability (polarization magnitude)

τ_0 relaxation time

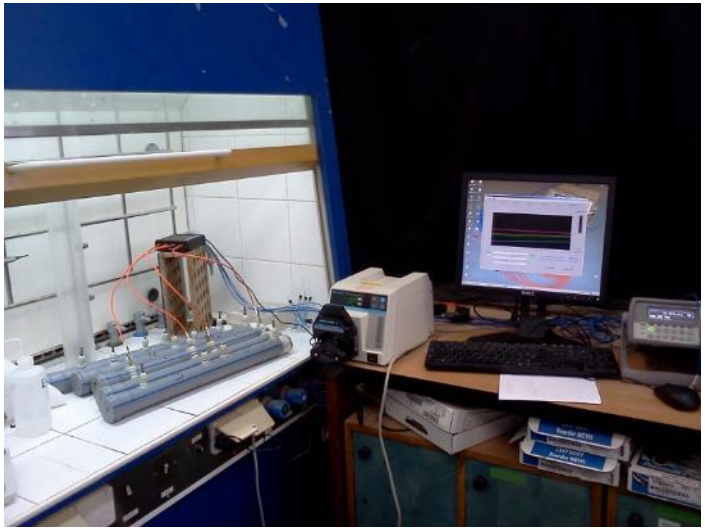
Fitting data to a double Cole-Cole model (L=2)
To obtain the parameters (Chen et al. 2008)



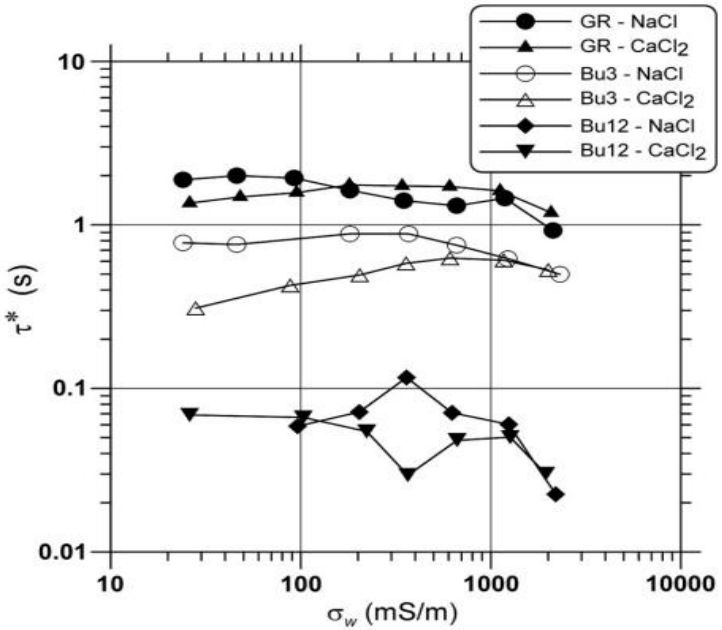
Other models exist: Debye, Pelton, Wurburg –changes in exponent

Materials and Methods

- Hamra soil was mixed with water and then with decane- hydrocarbon with very low water solubility (0.052 mg/L) –free phase.
- Clean and three decane contaminated treatments (0.8%, 1.6%, 3.16% w/w).
- The soil was rested for a five days
- Packing in horizontal PVC columns
- Electrical measurements
- Temporal SIP measurements for packed samples
- Soil solution chemical measurements



Previous works

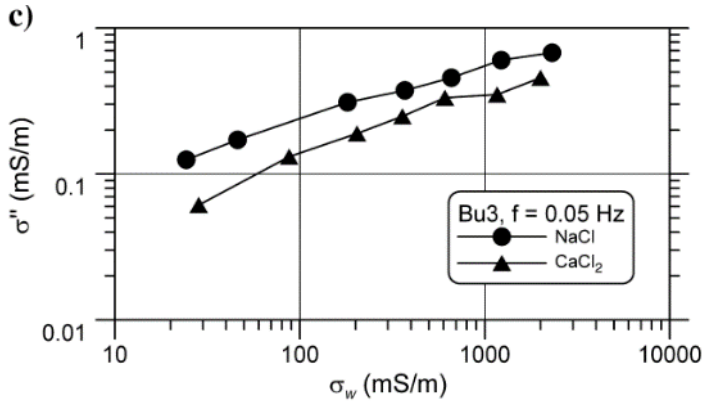


Change in relaxation time due to changes in solution chemistry and soil type.

Saturated.

$$\tau = l^2 / 2D$$

- The imaginary part of the complex conductivity behaves differently for different electrolytes.
- An increase of σ" is observed with rising salinity.



Weller et al. 2011

This study

Cations have different adsorption equilibrium constants, capacities, valence and ion mobility at the solid surface.

The electrical signature of soil changes between different surface adsorbed cations

Goal

Examine the ability to use SIP as an non-invasive identifying tool of the inorganic species composition of soil