Detection of Silver Nanoparticles in Vadose Zone Environments using Complex Conductivity Measurements

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Introduction

- Nanoparticles production and use has increased tremendously in recent years.
- In particular, silver nanoparticles (Ag NPs) are among the most widely used metal based engineered nanoparticles nowadays.
- The introduction of AgNPs into the vadose zone environment serves as a continued source of contamination to groundwater and associated receptors at nearly all environmental contaminated sites.

Introduction

- Early detection of AgNPs in the vadose zone can result in faster and less costly remediation.
- Therefore, there is a demand for the development of sensitive techniques to detect their presence and transport in the subsurface in conjunction with traditional soil and fluid sampling.
- Geophysical methods, specifically complex conductivity measurements, have shown to be sensitive to the presence of metals and subsurface contaminants.

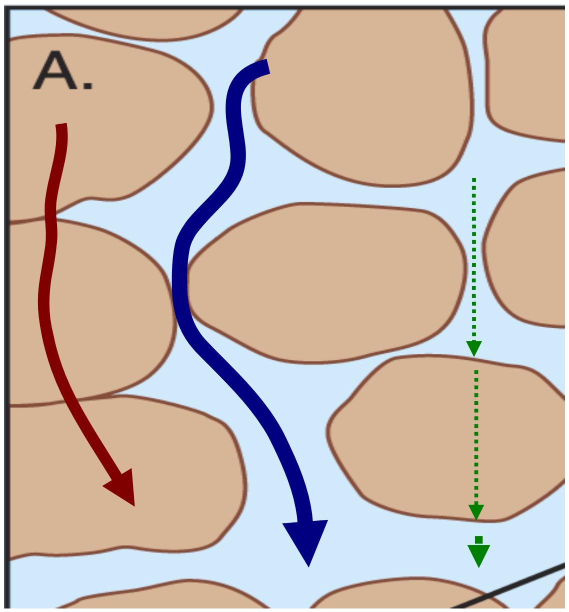
Objectives

- Laboratory experiments were conducted to investigate the complex conductivity response of silver nanoparticles (AgNPs) in sand columns under vadose zone conditions with different:
  - moisture content (0-30%),
  - nanoparticle concentrations (0-10 mg/g),
  - fluid chemistry (0.0275 and 0.1000 S/m),
  - lithology (sand and sand+clay), and
  - grain size diameters of AgNPs (35, 90-210 and 1250-2500 nm).

Electrical conduction in porous media

Electric current flow through a medium:

- ***electrolytic***; ionic conduction via an electrolyte (σ_{el})
- ***electronic***; electron conduction e.g. in metals (σ_{elc})
- ***interfacial***; charge storage (polarization) and charge loss (conduction) at electrochemical interfaces within porous media (σ^*_{int})

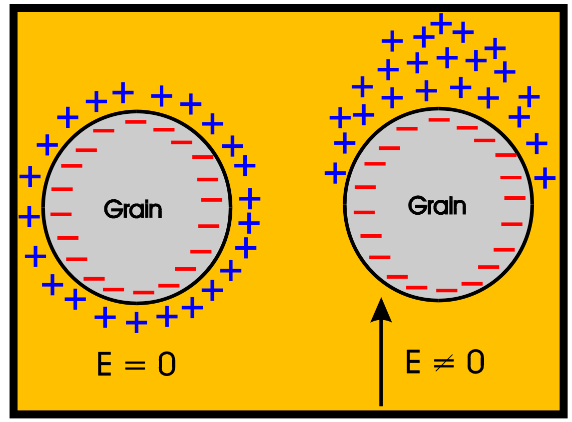


Complex Conductivity

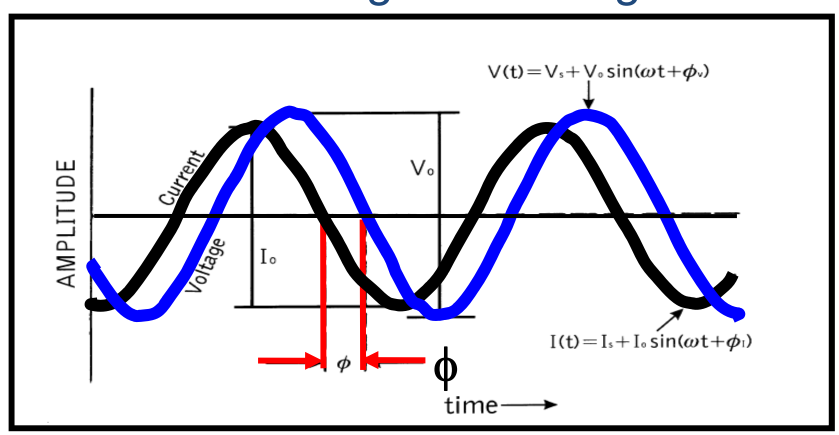
Induced polarization phenomenon

- Polarization:
  [1] redistribution of ions within electrical double layer of interconnected pore surface following application of electric current
  [2] relaxation of ions upon current termination:
  measured with time-domain IP equipment

  in frequency domain phase shift (*f*) between voltage & current waveforms



Simple schematic for polarization of electrical double layer of interconnected pore surface around a single mineral grain



Measured Quantities of Complex Conductivity

- **Impedance conductivity** $|\sigma|$
- **Phase** φ

$$\varphi = \tan^{-1}\left(\frac{\sigma''}{\sigma'}\right) \cong \frac{\sigma''}{\sigma'}$$

$$\sigma' = |\sigma| \cos\varphi$$

$$\sigma'' = |\sigma| \sin\varphi$$

In-phase conductivity

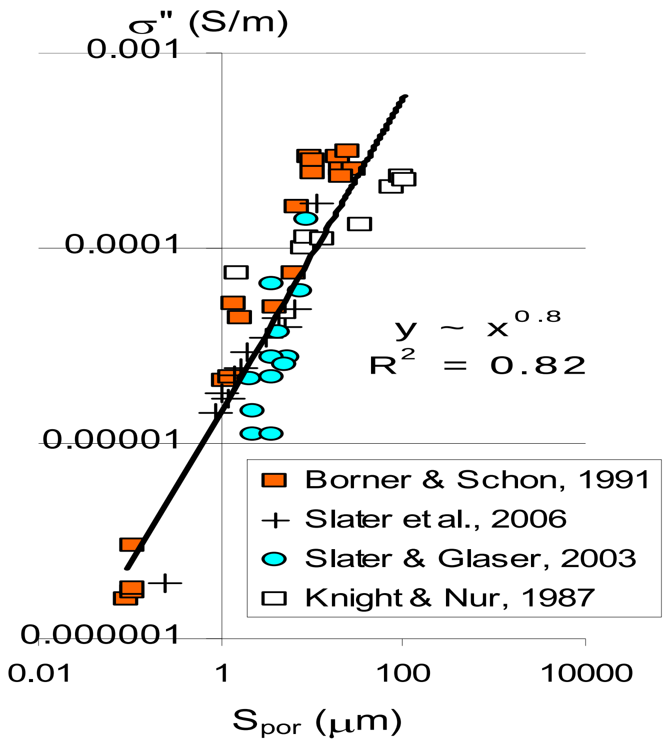
Sensitive to fluid chemistry and contains an electrolytic and interfacial component

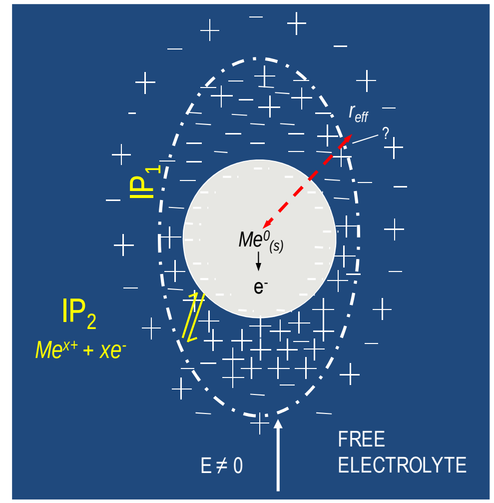
Quadrature conductivity

Sensitive to physicochemical properties at fluid-grain interface (e.g., ***surface area ,***surface charge density, ionic mobility,, and tortuosity)

Nanoparticles and Complex Conductivity

The complex conductivity or spectral induced polarization (SIP) method was originally developed and used to locate disseminated metallic mineral deposits





Metallic polarization dramatically enhanced IP effects

$\sigma' = f(\sigma_{el},\ \sigma_{elc},\ \sigma'_{int})$

$\sigma'' = \sigma''_{int}$

σ_{el} = conductivity of interconnected, fluid-filled pore space

σ_{elc} = electronic conduction through metal minerals (e.g. Fe^0)

σ^*_{int} =conduction/polarization at mineral/electrolyte interfaces

Credential- Lee Slater-Rutgers

Materials

AgNPs

Silica sand (Ottawa)
D50 = 200 ± 10 μm
Porosity = 0.45 ± 0.02

Clay (kaolinite) powder

Nanostructured & Amorphous Materials, Inc.

Grain size
35, 90-210 & 1500-2500 nm

Specific surface area
30-50, 2.40-4.42 & 0.4-0.8 m^2/g

Artificial Ground Water (AGW)
(Abdel Aal et al., 2009)
A (0.0275 S/m)
B (0.1000 S/m)
pH (7.1)

Experimental Setup

Experiments

1. **EFFECT OF SATURATION & AgNPs CONC.**

   Fine sand + AGW (0.0275 S/m) + different concentration of AgNPs (90-210 nm) (0, 2, 4, 6 , 8, 10 mg/g) + different water saturation (0.05, 0,10, 0.15, 0.20, and 0.30)

1. **EFFECT OF FLUID CHEMISTRY**

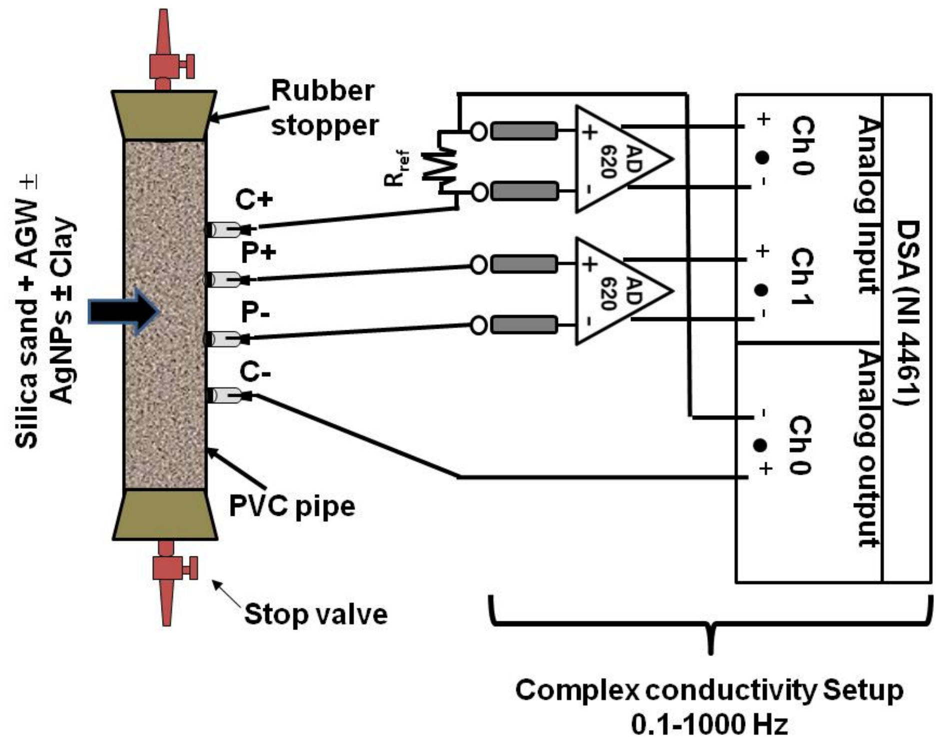
   Fine sand + AGW (0.0275 S/m or 0.1000 S/m) at 0.15 saturation ± AgNPs (90-210 nm and 6 mg/g)

1. **EFFECT OF LITHOLOGY**

   Fine sand ± clay + AGW (0.0275 S/m) at 0.15 saturation ± AgNPs (90-210 nm and 6 mg/g)

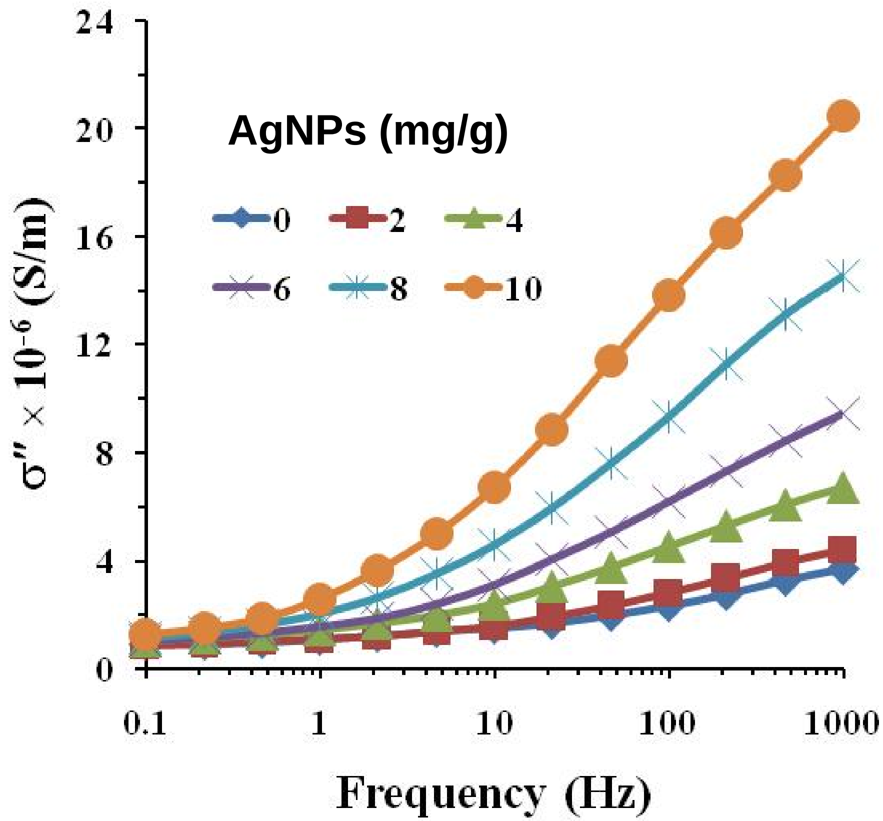
1. **EFFECT OF AgNPs GRAIN DIAMETERS**

   Fine sand + AGW (0.0275 S/m) at 0.15 saturation + AgNPs (35 nm, 90-210 nm and 1250-2500 nm)

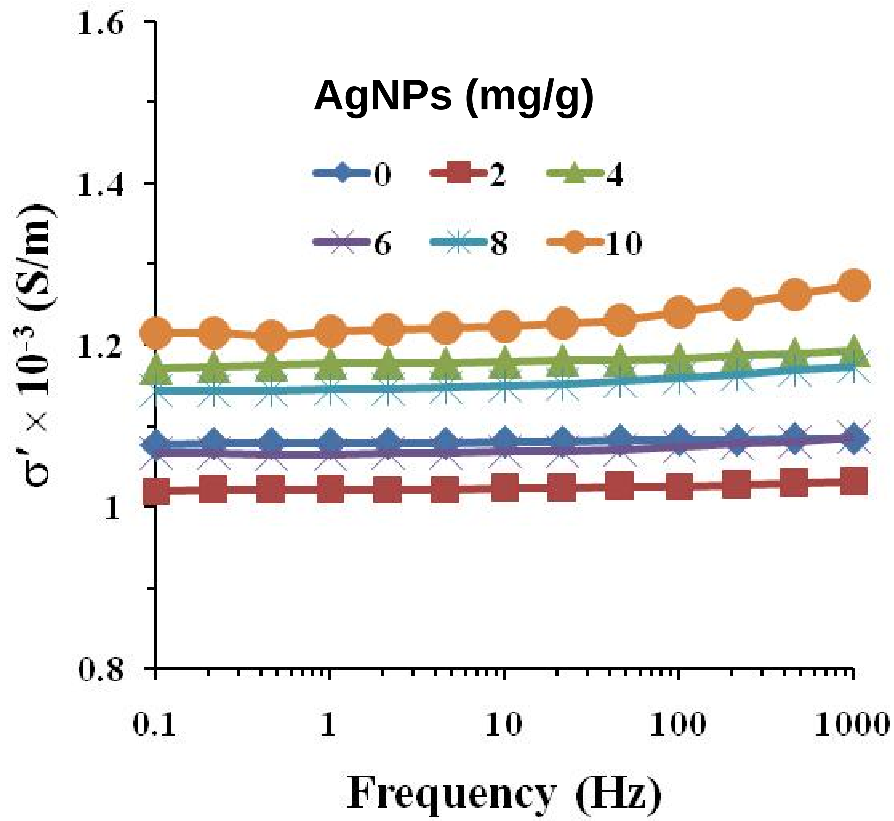


Results

Example of complex conductivity spectra of different AgNPs (90-210 nm) concentration in 15% partially saturated sand.



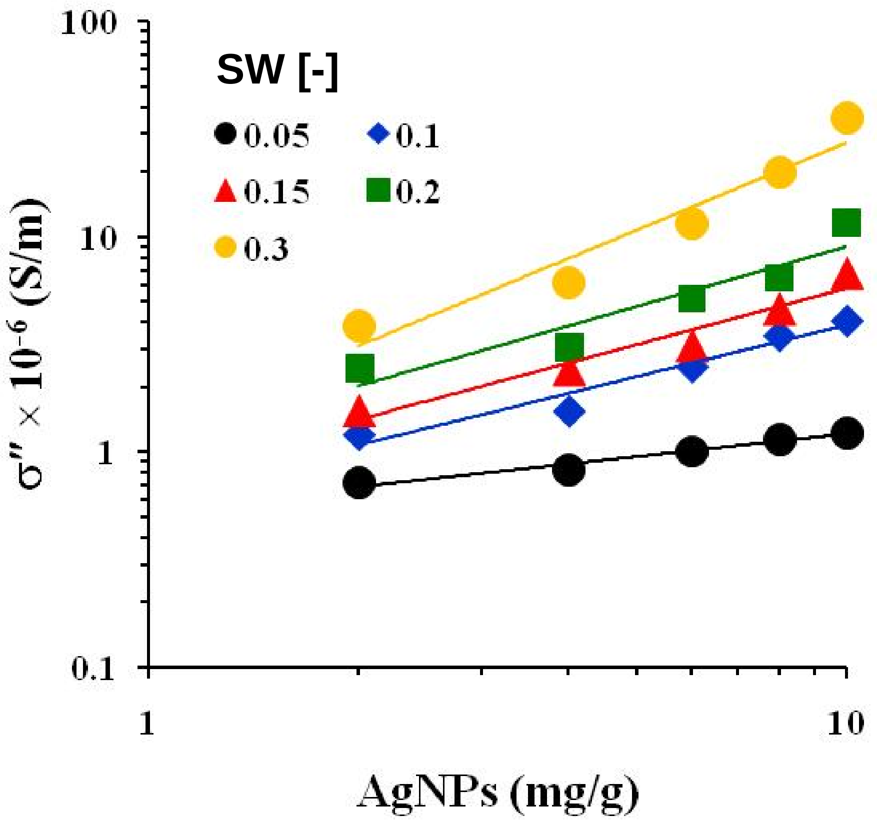
Quadrature conductivity



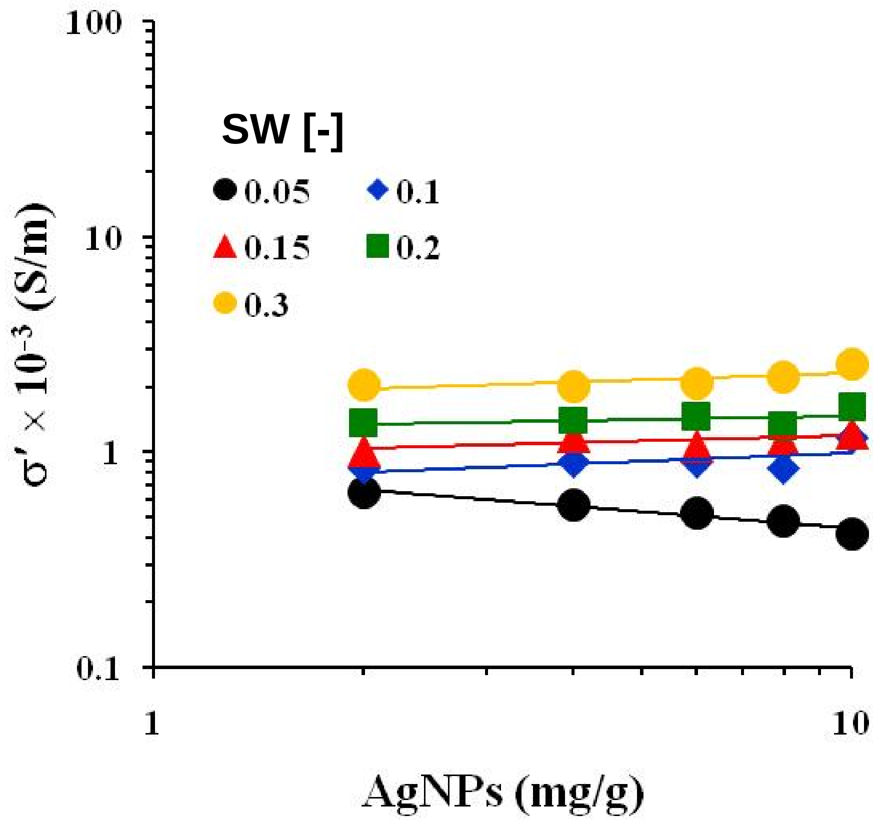
In-phase conductivity

Results

Complex conductivity response at 10 Hz of different AgNPs concentrations at different water saturation



Quadrature conductivity



In-phase conductivity

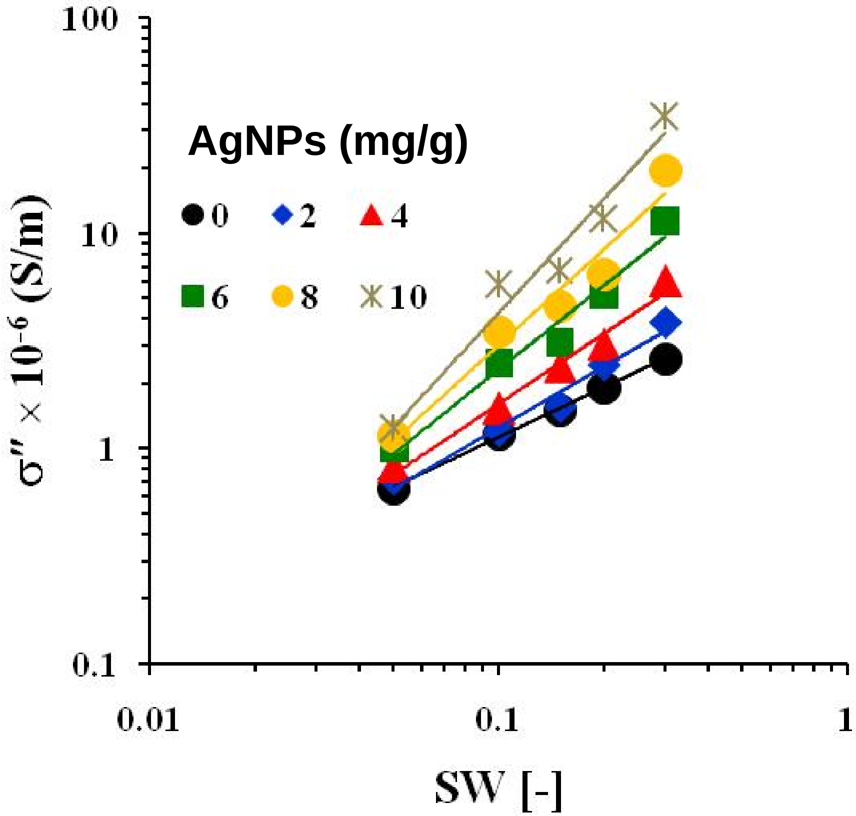
Results

Summary of power law fitted equations and correlation coefficients (R^2) for σ″ and σ′ at 10 Hz as a function of AgNPs concentrations at different water saturation.

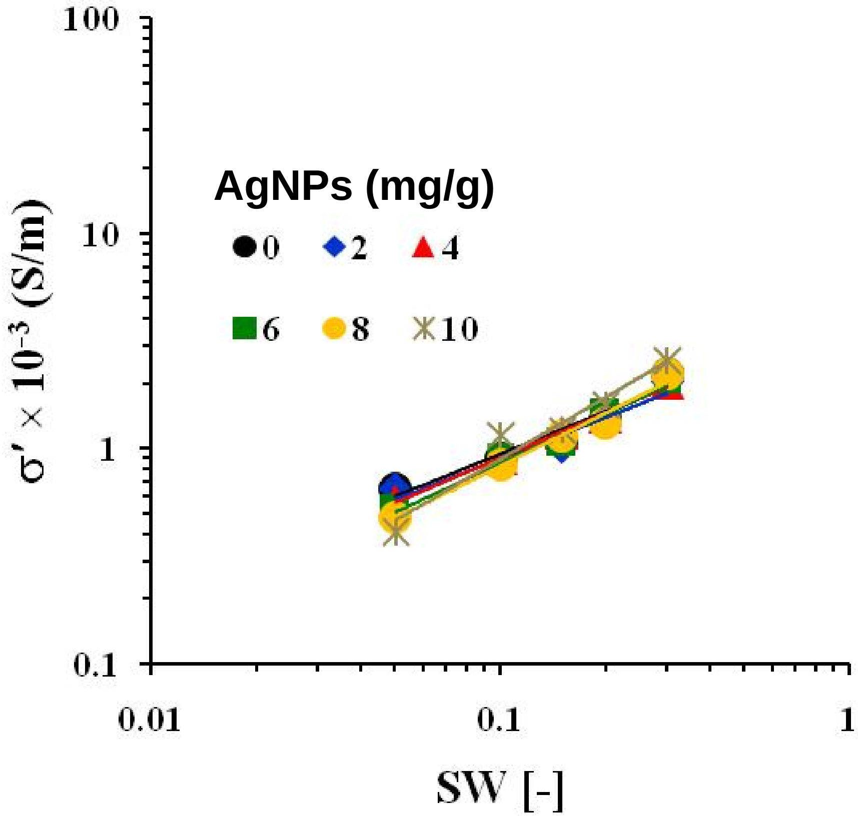
SW [-]	σ″ Fitted Equation	R^2	σ′ Fitted Equation	R^2
0.05	$\sigma'' \times 10^{-6} = 0.541\, Ag\, NP_{(mg/g)}^{0.353}$	0.97	$\sigma' \times 10^{-3} = 0.794\, Ag\, NP_{(mg/g)}^{-0.256}$	0.94
0.10	$\sigma'' \times 10^{-6} = 0.618\, Ag\, NP_{(mg/g)}^{0.798}$	0.95	$\sigma' \times 10^{-3} = 0.742\, Ag\, NP_{(mg/g)}^{0.128}$	0.36
0.15	$\sigma'' \times 10^{-6} = 0.776\, Ag\, NP_{(mg/g)}^{0.867}$	0.95	$\sigma' \times 10^{-3} = 0.980\, Ag\, NP_{(mg/g)}^{0.0.084}$	0.53
0.20	$\sigma'' \times 10^{-6} = 1.077\, Ag\, NP_{(mg/g)}^{0.0.920}$	0.88	$\sigma' \times 10^{-3} = 1.298\, Ag\, NP_{(mg/g)}^{0.056}$	0.21
0.30	$\sigma'' \times 10^{-6} = 1.216\, Ag\, NP_{(mg/g)}^{1.349}$	0.93	$\sigma' \times 10^{-3} = 1.792\, Ag\, NP_{(mg/g)}^{0.116}$	0.55

Results

Complex conductivity response at 10 Hz of different water saturation at different AgNPs concentrations



Quadrature conductivity



In-phase conductivity

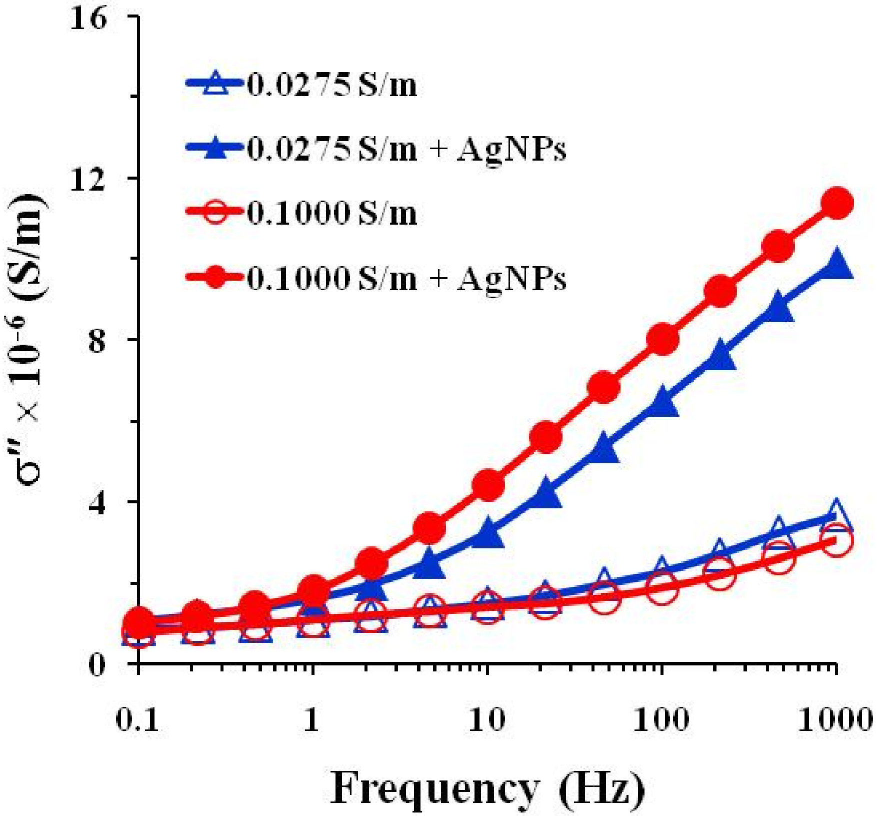
Results

Summary of power law fitted equations and correlation coefficients (R^2) for σ″ and σ′ at 10 Hz as a function of water saturation at different AgNPs concentration.

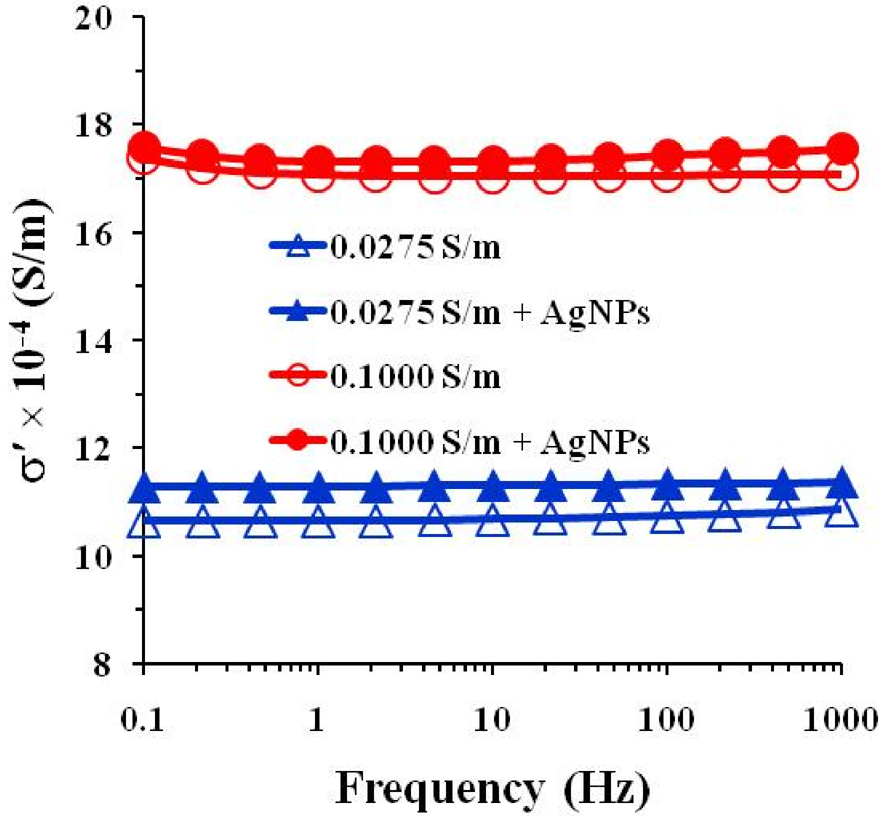
Ag NP (mg/g)	σ″ Fitted Equation	R^2	σ′ Fitted Equation	R^2
0	$\sigma'' \times 10^{-6} = 6.505\, SW_{[-]}^{0.762}$	0.99	$\sigma' \times 10^{-3} = 4.175\, SW_{[-]}^{0.649}$	0.93
2	$\sigma'' \times 10^{-6} = 10.618\, SW_{[-]}^{0.928}$	0.97	$\sigma' \times 10^{-3} = 3.828\, SW_{[-]}^{0.628}$	0.94
4	$\sigma'' \times 10^{-6} = 19.317\, SW_{[-]}^{1.076}$	0.98	$\sigma' \times 10^{-3} = 4.476\, SW_{[-]}^{0.695}$	0.99
6	$\sigma'' \times 10^{-6} = 44.828\, SW_{[-]}^{1.287}$	0.97	$\sigma' \times 10^{-3} = 4.872\, SW_{[-]}^{0.753}$	0.99
8	$\sigma'' \times 10^{-6} = 88.165\, SW_{[-]}^{1.463}$	0.96	$\sigma' \times 10^{-3} = 5.44\, SW_{[-]}^{0.817}$	0.98
10	$\sigma'' \times 10^{-6} = 234.660\, SW_{[-]}^{1.738}$	0.96	$\sigma' \times 10^{-3} = 8.018\, SW_{[-]}^{952}$	0.95

Results

Effect of fluid chemistry in the presence and absence of AgNPs (90-210 nm and 6 mg/g) in 15 % partially saturated sand



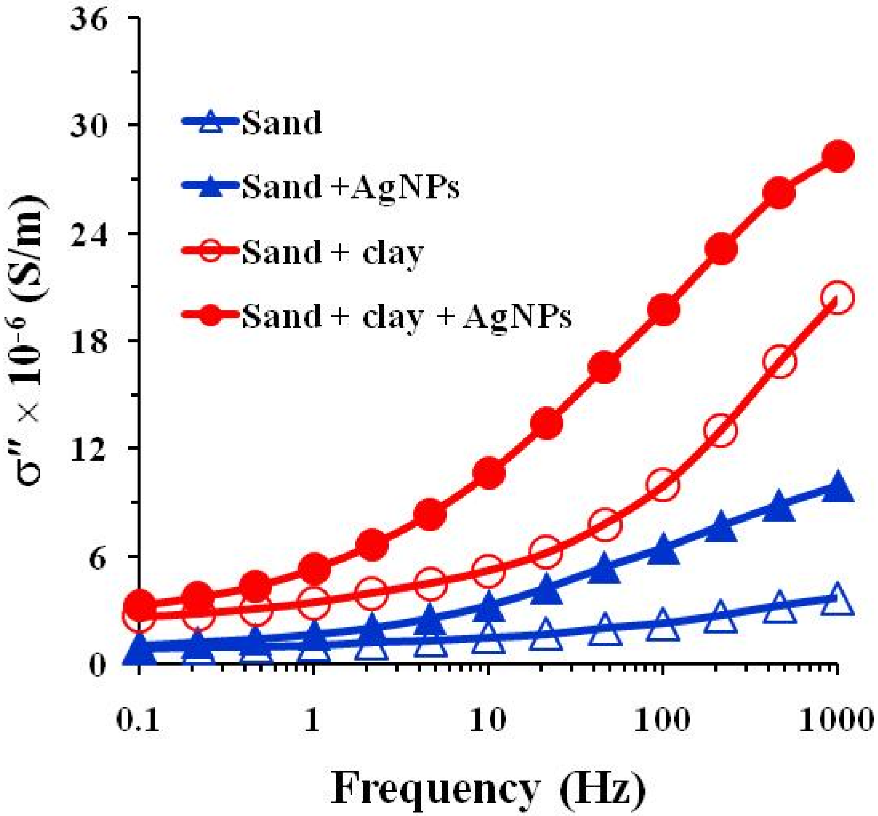
Quadrature conductivity



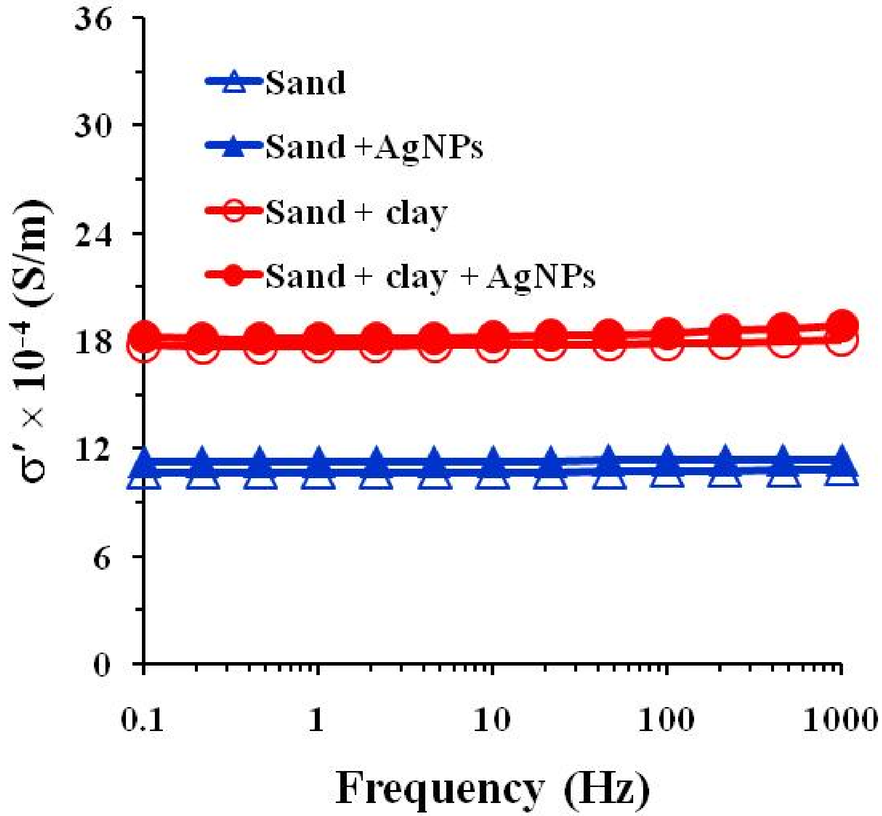
In-phase conductivity

Results

Effect of Lithology in the presence and absence of AgNPs (90-210 nm and 6 mg/g) with 15 % water saturation



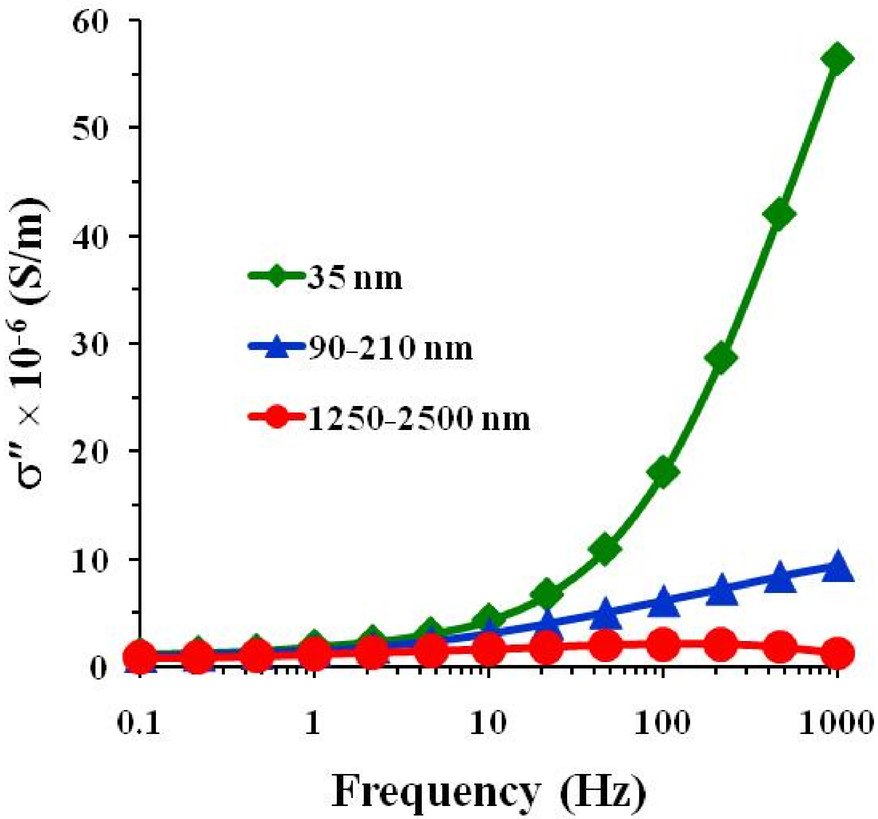
Quadrature conductivity

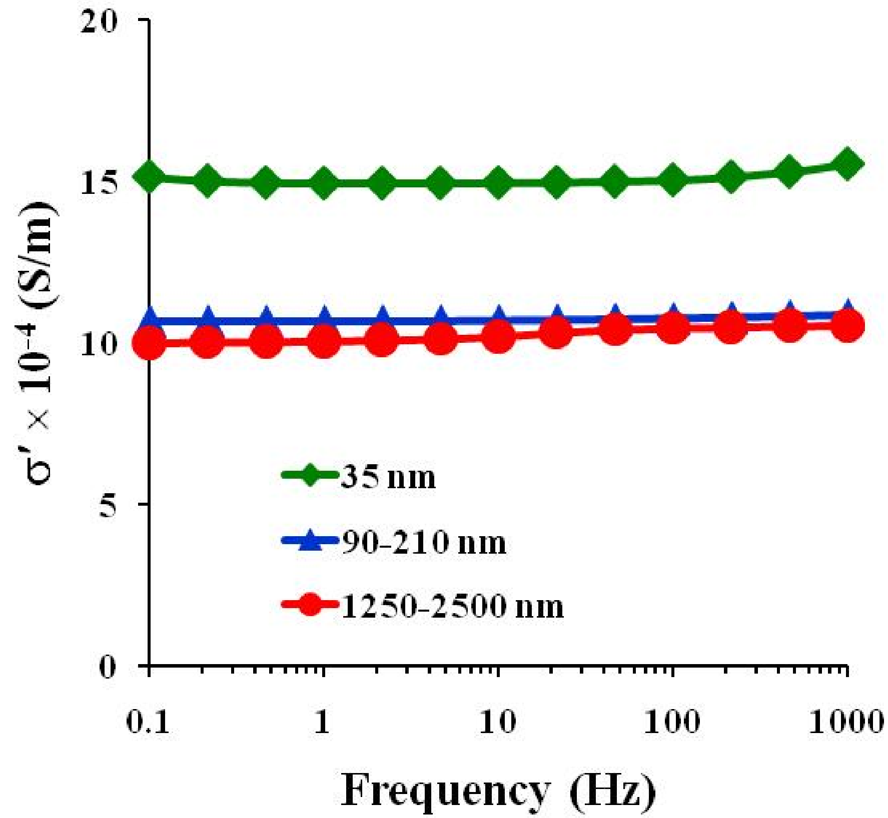


In-phase conductivity

Results

Effect of grain diameters of AgNPs (6 mg/g) in 15% partially saturated sand





Quadrature conductivity

In-phase conductivity

Summary & Conclusions

- At different water saturation the quadrature conductivity increased by one order of magnitude with increasing concentration of AgNPs with insignificant changes in the in-phase conductivity.

- At different concentrations of Ag nanoparticles the magnitude of the quadrature and in-phase conductivity components increased by one and half order and one order of magnitude, respectively.

- Estimation of AgNPs concentration can be obtained from the strong power law equations derived from the correlation between quadrature conductivity component and AgNPs concentrations.

Summary & Conclusions

- The addition of the silver nanoparticles increases the magnitude of all complex conductivity parameters being higher for the highest fluid conductivity (0.1000 S/m) and sandy clay mixture.

- The magnitude of the complex conductivity parameters increased with decreasing grain size diameters of AgNPs due to the increase in surface area.

- Our results demonstrate that the complex conductivity measurements are very sensitive to the presence of AgNPs in partially saturated porous media which potentially could be used in guiding the remediation processes of such contaminants within the vadose zone.

Questions

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