Advancing Spectral Induced Polarization for Near Surface Geophysical Characterization

By

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ABSTRACT OF THE DISSERTATION

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Spectral induced polarization (SIP) is an electrical geophysical technique that non-invasively characterizes subsurface environmental processes by measuring the complex electrical conductivity. Complex conductivity, which includes a real component representing the ability of electrical conduction and an imaginary component representing the ability of electrical charge storage (i.e., polarization), provides distinct insights into the interfacial properties in porous materials. This dissertation focuses on the improvement of data acquisition, data interpretation, and hydrological applications of the SIP technique.

First, a novel correction method was developed to remove the laboratory SIP measurement errors at kHz frequencies. These errors were accurately predicted by an electrical circuit model considering the parasitic capacitive coupling effects of the measurement system. The corrected SIP spectra of various earth material samples show excellent agreement with the theory. This study sheds light on the research on kHz range electrical properties which are important for understanding the physicochemical properties of small particles yet overlooked due to unrecognized errors in previous studies.
Secondly, negative induced polarization (IP) effects were investigated to improve the data interpretation of SIP. Fundamental theory was developed to quantitatively explain the negative IP effects, which are associated with sensitivity of resistivity measurements and subsurface heterogeneity. Comprehensive studies including numerical modeling, electrical circuit modeling, and sandbox experiments were performed to demonstrate the occurrence and control factors of negative IP effects. This work highlights the importance of including negative IP data, that were normally discarded as measurement errors, in the inversion or interpretation.

Finally, a novel field SIP methodology was developed to characterize the physical properties of streambed sediments in river corridors. Synthetic modeling using a 1D analytical model illustrates the influence of water layer depth and conductivity on the field SIP measurements made at the streambed-stream water interface. Field SIP measurements along a landfill-impacted river reveal discrete streambed zones with enhanced bulk surface area generally corresponding to anoxic groundwater discharge zones with high concentrations of fine-grained iron oxide precipitates. This work highlights the advantage of the SIP method and its potential for studying the river dynamics and conditions.
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Chapter 1 Introduction

1.1 Background and overview

Geophysical methods are powerful techniques that non-invasively characterize the Earth subsurface. Similar to medical imaging, geophysical techniques diagnose the Earth by sending signals from the surface into the Earth’s body and receiving returned signals. Based on the desired Earth information, different geophysical techniques are used as each geophysical signal has its specific target. For example, electrical methods examine the fluid properties by measuring the ability of electrical conduction; seismic methods reveal the Earth structure by recording the travel of seismic waves; magnetic methods identify the metallic minerals by sensing the anomalous magnetic spots (Butler 2005). Oil and mining explorations rely on geophysical methods as the non-invasive and high-resolution sensing of the subsurface highly reduces the risk of waste drillings, which saves enormous money and time. These advantages also make geophysics a promising and attractive tool to study near surface environmental problems. In particular, galvanic electrical geophysical methods including the direct current method and induced polarization play important roles in environmental science research (Binley & Slater 2020). These methods have unique sensitivity to the subsurface structure and pore fluid chemistry, which improves the delineation of various biogeochemical and hydrological processes.

The direct current (DC) method is one of the most commonly used geophysical techniques in environmental science. This method injects DC into the ground and determines the DC electrical conductivity (or its inverse, electrical resistivity) of the subsurface. Electrical conductivity quantifies the ability of electrical conduction, which in most Earth materials,
is dominated by electrolytic conduction via conductive fluids in the interconnected pore space (S. Ward 1988, Glover 2015). Therefore, the DC method is very sensitive to the pore fluid properties and is suitable for characterizing features/processes involving distinct water content and/or pore water conductivity (Butler 2005, Binley 2015). Previous studies have shown great potentials of the DC method in monitoring various environmental processes such as contaminant migration (Clément et al, 2010), groundwater remediation (Johnson et al. 2015), and groundwater-surface water interaction (Nyquist et al. 2008, A. Ward et al. 2010). In addition to water content and conductivity, DC conductivity is also highly influenced by textural and geological properties such as porosity, tortuosity, and clay content (S. Ward 1988, Glover 2015). This makes the DC method potentially reveal the variations of subsurface structure and geological settings, but meanwhile highlights the large uncertainty of the DC method as changes in DC conductivity could result from multiple factors.

As an extension of the DC method, induced polarization (IP) measures both electrical conduction and polarization, providing additional information for the interpretation of the subsurface (Sumner 1976, Binley 2015, Binley & Slater 2020). The terminology ‘induced polarization’ refers to the phenomenon that the bounded electric charges at the solid-fluid interface displace (i.e., ‘polarization’) instead of moving freely under an applied electric field (i.e., ‘induced’). The polarization strength can be roughly analogized to the electrical capacitance in electrical engineering and represents the ability of the Earth materials to temporarily store the electric current. IP is measured as either a chargeability in time-domain or a complex electrical conductivity in frequency-domain, where the latter case is
specifically named as spectral induced polarization (SIP) or complex conductivity method (Kemna et al. 2012). Compared to the DC method, SIP is exclusively sensitive to the properties governing solid-fluid interfacial behaviors such as cation exchange capacity (Vinegar & Waxman 1984), surface area (Börner & Schön 1991), grain/pore size (Schwarz 1962, Scott & Barker 2003) and metallic mineral content (Pelton et al. 1978). Therefore, SIP has been widely applied for mapping changes in lithology (Slater & Lesmes 2002a), estimating hydraulic conductivity (Binley et al. 2005), and monitoring mineralization and microbial activities in various biogeochemical processes (Ntarlagiannis et al. 2005, Williams et al. 2005).

Like all other geophysical techniques, successful applications of SIP rely on accurate data acquisition, robust data processing, and reliable interpretation. With decades of development, our understanding of the methodology and mechanism of the SIP technique has improved and continues to evolve. This dissertation will address a variety of topics that remain challenging to improve the data acquisition and interpretation of the SIP technique for near surface characterization.

1.2 Research objectives

This dissertation aims to explore the challenges covering various topics of SIP. After Chapter 2 introduces the background of SIP, Chapter 3, 4, and 5 describe the main research on SIP that improves the data acquisition, interpretation, and novel application, respectively. Chapter 3 proposes a novel correction method that improves the laboratory SIP measurement accuracy at high frequencies (kHz range). Chapter 4 studies the negative
induced polarization effects in SIP measurements to improve the understanding of SIP signals and interpretation. Chapter 5 investigates the application of SIP in river corridors to map anoxic groundwater discharge zones that are considered as biogeochemical hot spots. In addition to the research work on the SIP method, research on the evaluation of riverbed magnetic susceptibility for mapping biogeochemical hot spots was also conducted. This magnetic susceptibility research is not presented as a main chapter but included in Appendix A. Below are the detailed research objectives of each main chapter.

(a) Extend accurate laboratory SIP measurements into the kHz frequency range (Chapter 3).
   a1. Establish a novel model to accurately simulate high frequency phase errors caused by the interactions between the parasitic capacitive coupling and the sample holder.
   a2. Develop a correction method using the established model to remove laboratory SIP measurement errors at high frequencies and verify it using electric circuit and fluid samples with known SIP signals.
   a3. Apply the correction method to various Earth materials to acquire high quality SIP spectra at high frequencies and propose new interpretations based on the improved data.

(b) Reveal the significance of negative induced polarization (IP) effects in field SIP measurements (Chapter 4).
   b1. Develop a theory that mathematically proves the occurrence of error-free negative IP data (i.e., positive apparent phase).
   b2. Demonstrate the negative IP effects and investigate the factors controlling negative IP using numerical modeling.
b3. Propose a physical explanation of negative IP effects using electric circuit models.

b4. Examine the negative IP effects using sandbox experiments to support the observations from theory and numerical modeling.

(c) Investigate the application of SIP in a water environment to non-invasively characterize the streambed sediment physical properties (Chapter 5).

c1. Demonstrate the controls of sediment properties on various SIP parameters by laboratory analysis and SIP measurements.

c2. Investigate the influence of the surface water layer depth and electrical conductivity on streambed SIP using numerical modeling.

c3. Perform field SIP measurements along a landfill-impacted coastal stream to map anoxic groundwater discharge zones where high surface area Fe oxides are precipitated in shallow streambed sediments.
Chapter 2  Background of Spectral Induced Polarization

2.1  Complex conductivity in SIP

The electrical conduction and displacement in a linear, homogeneous and isotropic material can be described as (B. Fuller & Ward 1970, Vinegar & Waxman 1984),

\[ \mathbf{J} = \sigma^* \mathbf{E} = \omega \varepsilon^* \mathbf{E}, \]  

(2.1)

where \( \mathbf{J} \) is the current density, \( \mathbf{E} \) is the time harmonic electric field, \( \omega \) is the angular frequency and \( \omega = 2\pi f \) where \( f \) is the frequency in Hz, \( \sigma^* \) is the effective complex conductivity, and \( \varepsilon^* \) is the effective complex dielectric permittivity. \( \sigma^* \) and \( \varepsilon^* \) are two frequency-dependent parameters that define the electrical properties in different ways. These parameters represent the effective electrical responses from multiple polarization mechanisms instead of referring to a specific mechanism (B. Fuller & Ward 1970, Vinegar & Waxman 1984). The SIP technique focuses on the electrical responses at a relatively low frequency range (1 mHz to tens of kHz), in which the term \( \sigma^* \) or its inverse, complex resistivity \( \rho^* \) is most commonly used,

\[ \sigma^* = |\sigma^*| e^{i\varphi_\sigma} = \frac{1}{\rho^*} = \frac{1}{|\rho^*|} e^{i(-\varphi_\rho)}, \]  

(2.2)

where \( |\sigma^*| \) and \( \varphi_\sigma \) are the complex conductivity magnitude and phase, respectively; \( |\rho^*| \) and \( \varphi_\rho \) are the complex resistivity magnitude and phase, respectively; \( i \) is the imaginary unit with \( i^2 = -1 \). Eq. (2.2) shows that \( |\sigma^*| \) is the inverse of \( |\rho^*| \), which is the same as the DC conductivity-resistivity relationship. \( \varphi_\sigma \) is the opposite of \( \varphi_\rho \). Earth materials have an intrinsic lossy electrical capacitance, making \( \varphi_\sigma > 0 \) and \( \varphi_\rho < 0 \). As a complex number parameter, \( \sigma^* \) can also be expressed in the rectangular form,
\[
\sigma^* = \sigma' + i\sigma'', \quad (2.3)
\]

\[
\sigma' = |\sigma^*| \cos \varphi_\sigma, \quad (2.4)
\]

\[
\sigma'' = |\sigma^*| \sin \varphi_\sigma, \quad (2.5)
\]

where \(\sigma'\) and \(\sigma''\) are the real and imaginary conductivity, respectively. For Earth materials with no or small amount of electronically conducting minerals, \(\varphi_\sigma\) is a small quantity (e.g., \(0 < \varphi_\sigma < 0.1\)), which gives \(\cos \varphi_\sigma \approx 1\) and \(\varphi_\sigma \approx \sin(\varphi_\sigma) \approx \tan(\varphi_\sigma) \approx \tan^{-1}(\varphi_\sigma)\). Therefore, we have the approximations

\[
\sigma' \approx |\sigma^*|, \quad (2.6)
\]

\[
\varphi_\sigma = \tan^{-1}\frac{\sigma''}{\sigma'} \approx \frac{\sigma''}{\sigma'}. \quad (2.7)
\]

The parameters \(\sigma'\) and \(|\sigma^*|\) represent the electrical conduction, which is equivalent to the DC electrical conductivity measured from the DC method. The parameters \(\sigma''\) and \(\varphi_\sigma\) represent the electrical polarization.

In SIP, \(\sigma^*\) data are presented as frequency dependent spectra. The measurement frequencies normally fall between 1 mHz and 45 kHz, although accurate data are often limited to low frequencies < 100 Hz. \(\sigma'\) and \(|\sigma^*|\) have little variations at various frequencies, whereas the \(\sigma''\) and \(\varphi_\sigma\) spectra could have different shapes, providing insights into the polarization of the materials. The polarization mechanisms in the SIP frequency range mainly include the electrochemical polarization and the Maxwell-Wagner polarization. Electrochemical polarization (the primary focus of SIP research) occurs due to the migration of charge carriers (ions, electrons) at the solid-fluid interfaces, which typically includes the electrical
double layer (EDL) polarization, membrane polarization and electrode polarization. The most fundamental shape of $\sigma''$ (or $\varphi_\sigma$) spectrum corresponding to electrochemical polarization is a relaxation curve defined by a Cole-Cole equation (Cole & Cole 1941), which shows a peak $\sigma''$ (or $\varphi_\sigma$) at frequency $f_{\text{peak}}$ (Figure 2.1a). The term ‘relaxation time’, defined as the inverse of $2\pi f_{\text{peak}}$, is often used to evaluate the location of the $\sigma''$ (or $\varphi_\sigma$) peak (Tarasov & Titov 2013). A longer/larger relaxation time means a polarization peak occurs at a lower frequency and vice versa. While the magnitude of the $\sigma''$ (or $\varphi_\sigma$) peak represents the polarization strength, the relaxation time indicates the characteristic length (related to particle or pore size) at which polarization occurs (Pelton et al. 1978, Revil, Koch, et al. 2012, Weller et al. 2016). A short relaxation time (hence a higher peak frequency) indicates a smaller characteristic length of polarization and vice versa. Natural Earth materials commonly have a wide range of grain/pore sizes, thereby exhibiting a broad or irregular relaxation curve consisting of numerous polarization peaks with various strengths (Figure 2.1b). In this case, the distribution of relaxation time and corresponding polarization strength and/or the integrated polarization strength across the frequency range (e.g., chargeability) are evaluated, for example, using multi Cole-Cole fitting or Debye decomposition approach (Nordsiek & Weller 2008, Breede et al. 2011). In cases where $\sigma''$ (or $\varphi_\sigma$) shows low frequency dependence (e.g., with a very broad relaxation), SIP data at a representative single frequency (e.g., 1 Hz) are frequently interpreted (Vinegar & Waxman 1984, Slater et al. 2006, Revil 2012). Maxwell-Wagner polarization occurs due to the charge accumulation at the interface between two phases with different dielectric permittivity and electrical conductivity (Chen & Or 2006). This polarization describes the dielectric behavior of multiphase mixtures and only becomes significant at high frequency
range (>100 Hz) of SIP measurements (Leroy et al. 2008). In practice, SIP data at high frequencies normally contain large measurement errors due to the leakage currents via capacitive coupling effects in the instrument, which makes it difficult to evaluate the Maxwell-Wagner polarization (Huisman et al. 2016, Wang & Slater 2019). The addition of high frequency errors and Maxwell-Wagner polarization often result in a dramatic increase of $\sigma''$ (or $\phi_\sigma$) towards the high frequency end of SIP measurements (Figure 2.1c), which obscures the signals from electrochemical polarization at high frequencies. Therefore, most SIP studies are restricted to low frequency range (<100 Hz), which limits the understanding of polarization from small particles/pores (e.g., clays, microbes, and nanoparticles). To improve the SIP measurement accuracy at high frequencies, Chapter 3 investigates the cause of measurement errors and develops a novel correction procedure, which may facilitate future SIP studies on high frequency polarization. Nevertheless, studies on the low frequency SIP have generated numerous theories, models, and laboratory observations, which improve the understanding of the relationships between SIP signals and various physicochemical properties. The most general findings from these studies will be introduced in the following section.

Figure 2.1. Conceptual examples of various SIP spectra. (a) A relaxation curve showing a pronounced peak. (b) A broad relaxation curve containing numerous peaks. (c) A relaxation curve showing a dramatic increase toward the high frequency end (dashed line).
2.2 SIP petrophysics and interpretation

The near surface Earth materials are mainly dominated by non-electronically conducting soil and rock matrix. The electrical responses of these porous media are established on the electrically conductive pore fluids and their interactions with solid phases. The complex conductivity \( \sigma^* \) (eq. 2.2) can be interpreted as the sum of an electrolytic conductivity \( \sigma_{el} \) and a surface complex conductivity \( \sigma_{surf}^* \) (Vinegar & Waxman 1984, Lesmes & Frye 2001, Weller et al. 2013),

\[
\sigma^* = \sigma_{el} + \sigma_{surf}^* = (\sigma_{el} + \sigma_{surf}') + i\sigma_{surf}'', \tag{2.8}
\]

where \( \sigma_{el} \) represents the electrolytic conduction through the fluids in the interconnected pores; \( \sigma_{surf}' \) and \( \sigma_{surf}'' \) are the real and imaginary parts of \( \sigma_{surf}^* \), which represent surface conduction and polarization occurring at the solid-fluid interfaces, respectively. Eqs. (2.3) and (2.8) show that the real conductivity \( \sigma' \) is contributed from both \( \sigma_{el} \) and \( \sigma_{surf}' \), whereas the imaginary conductivity \( \sigma'' \) is only attributed to \( \sigma_{surf}'' \). Considering a fully saturated medium, \( \sigma_{el} \) is expressed as (Archie 1942),

\[
\sigma_{el} = \frac{1}{F} \sigma_f = \Phi^m \sigma_f, \tag{2.9}
\]

where \( \sigma_f \) is the pore fluid electrical conductivity; \( F \) is the electrical formation factor; \( \Phi \) is the interconnected porosity and \( m \) is the cementation exponent indicating the tortuosity or connectedness of the pore network (Glover 2009). When \( \sigma_{surf}' \) is negligible, \( \sigma' \) is dominated by \( \sigma_{el} \), which is dependent on \( \sigma_f \). Therefore, variations in \( \sigma' \) (or DC conductivity) strongly indicate the change of \( \sigma_f \) when the geology and structures have little difference. However, \( \sigma_{surf}' \) can be important in presence of clay minerals, causing the interpretation of \( \sigma' \) contains
ambiguity as both $\sigma_{el}$ and $\sigma_{surf}'$ control $\sigma'$ (Börner et al. 1996). For example, a relatively higher $\sigma'$ may indicate either a higher fluid salinity (i.e., higher $\sigma_{el}$) or a higher clay content (i.e., higher $\sigma_{surf}'$). While it is difficult to directly determine $\sigma_{surf}'$ in the field, an empirical relationship $\sigma'' = 0.042 \sigma_{surf}'$ has been established using an extensive database of samples (Weller et al. 2013). Therefore, SIP measurements with the additionally acquired $\sigma''$ data compared to the DC method may reduce the ambiguity of the interpretation of $\sigma'$ or DC conductivity.

The polarization term $\sigma''$ or $\phi_\sigma$ has intrinsic associations with different physicochemical properties. Numerous studies using theories, models, and laboratory experiments have been conducted to investigate the mechanisms and petrophysics of SIP signals (e.g., Vinegar & Waxman 1984, Slater et al. 2006, Leroy et al. 2008, Revil 2012, Bücker & Hördt 2013, Weller & Slater 2015). Most studies have been focusing on the electrochemical polarization at low frequencies, which shows different behaviors for non-electronically conducting and electronically conducting minerals.

2.2.1 Polarization of non-electronically conducting materials

In Earth materials with water, naturally charged mineral surface attracts ions from pore water, which form an EDL consisting of a Stern (fixed) layer and a diffuse layer (Lesmes & Frye 2001, Glover 2015). The Stern (fixed) layer has ions strongly bonded at the interface between mineral and water, while the diffuse layer has loosely bonded ions extending into free ions in the pore water. The polarization results from the migration of ions in the EDL under an applied electric field (Kemna et al. 2012). SIP theories and
petrophysical models of non-electronically conducting minerals were developed based on $\sigma''$, which has much weaker dependence on the pore fluid conductivity compared to $\phi_\sigma$ (Vinegar & Waxman 1984). Data of $\sigma''$ at a single frequency is often interpreted as $\sigma''$ spectra commonly show weak frequency dependence for non-electronically conducting minerals (Vinegar & Waxman 1984). The parameters determining $\sigma''$ can be summarized into three categories: (1) micro-scale parameters defining the EDL properties such as surface charge density, surface charge mobility and relative fraction of counterions in the Stern and diffuse layers; (2) parameters defining the sample structural properties such as electrical formation factor, porosity, solid phase density; (3) macro-scale parameters defining bulk sample physicochemical properties such as cation exchange capacity, grain size distribution, and specific surface area (Lesmes & Morgan 2001, Slater et al. 2006, Revil 2012, Revil, Koch, et al. 2012, Weller & Slater 2015). Pore water conductivity influences $\sigma''$ by altering the EDL properties (Revil & Skold 2011). Increasing pore water conductivity will increase $\sigma''$ due to the increased surface charge density (i.e., the quantity of charge per unit area), and then decrease $\sigma''$ due to the reduced charge mobility (i.e., the ability of charge movement) under too high pore water conductivity conditions (e.g., 1 S/m) (Lesmes & Frye 2001, Weller et al. 2011). However, these influences of pore water conductivity on $\sigma''$ are weak due to the limited variations in EDL properties. In contrast, pore water conductivity strongly controls $\sigma'$ and hence $\phi_\sigma$ according to Eq. (2.7). Therefore, $\sigma''$ is a robust parameter that infers the physical properties of the porous media excluding influences from small variations (e.g., < 10 times) in pore water conductivity. By assuming various parameters determining $\sigma''$ to be constants, different mechanistic and empirical models have been proposed to describe the linear dependence of $\sigma''$ on cation exchange
capacity (Vinegar & Waxman 1984, Revil 2012), specific surface area (Börner & Schön 1991, Revil 2012), specific surface area per unit pore volume ($S_{por}$) (Börner et al. 1996, Weller et al. 2010, 2015) and $S_{por}$ normalized by formation factor (Weller & Slater 2012, 2019, Niu, Prasad, et al. 2016). In addition to models focusing on single frequency $\sigma''$, models considering the frequency dependent $\sigma''$ spectrum were also developed and evaluated. These models associate the $\sigma''$ relaxation time (or relaxation time distribution) to the characteristic pore/grain size (or pore/grain size distribution) (Lesmes & Morgan 2001, Bücker & Hördt 2013), which facilitate the prediction of permeability (Revil, Binley, et al. 2015, Robinson et al. 2018) and monitoring of grain/pore size changes associated with mineralization and microbial growth (Slater et al. 2007, Leroy et al. 2017).

2.2.2 Polarization of electronically conducting materials

Electronically conducting minerals such as pyrite, graphite and magnetite generally exhibit stronger polarization and more pronounced relaxation peaks (known as electrode polarization). Models and laboratory experiments studying the SIP of these minerals have shown that $\phi_{\sigma}$ is the characteristic polarization parameter that is less impacted by pore fluid conductivity than $\sigma''$. Considering a low-polarizable matrix (e.g., clean sands) containing diluted disseminated metallic particles (i.e., metallic particles do not contact each other) with uniform size, the low frequency $\phi_{\sigma}$ spectrum is expected to have a similar shape as Figure 2.1a. Different from sand and clay minerals, the relatively stronger and narrower relaxation spectrum of metallic particles make it more meaningful to interpret the $\phi_{\sigma}$ peak instead of the single frequency data. Previous studies have resulted in three main general findings: (1) the magnitude of $\phi_{\sigma}$ peak increases with increasing metallic particle content
and is not significantly influenced by pore fluid conductivity; (2) the relaxation time decreases with increasing fluid conductivity and decreasing metallic particle size; (3) the magnitude of $\sigma''$ peak increases with increasing pore fluid conductivity (Wong 1979, Slater et al. 2005, Gurin et al. 2015, Revil, Abdel Aal, et al. 2015, Revil, Florsch, et al. 2015, Placencia-Gómez & Slater 2016). Although studies on electrode polarization were originally for mining exploration, it becomes more important in near surface studies to understand the SIP signatures of metallic contaminants and metallic minerals from biogeochemical reactions (Williams et al. 2005, Slater et al. 2007).

2.3 SIP data acquisition

2.3.1 Laboratory measurements

The principle of laboratory SIP measurements is illustrated using a four-electrode cylindrical sample holder packed with fully saturated homogeneous unconsolidated samples (Figure 2.2a). A stimulus sinusoidal current $\tilde{I}$ is injected through a packed sample via two current electrodes (A and B), while the resultant sinusoidal voltage drop $\Delta \tilde{U}$ through a segment of the sample is recorded via two potential electrodes (M and N). According to Ohm’s law, the impedance $Z'$ of the sample between M and N is determined as (Figure 2.2b):

$$ Z' = |Z'|e^{i\varphi_z} = \frac{\Delta \tilde{U}}{\tilde{I}} = \frac{|\Delta \tilde{U}| \sin(\omega t + \varphi_{\Delta U})}{|\tilde{I}| \sin(\omega t)}, \quad (2.10) $$

where $|Z'|$ and $\varphi_z$ are the impedance magnitude and phase respectively, $\omega$ is the angular frequency, $t$ is time, $|\tilde{I}|$ is the current amplitude, $|\Delta \tilde{U}|$ is the voltage amplitude and $\varphi_{\Delta U}$ is the phase shift of $\Delta \tilde{U}$ relative to $\tilde{I}$ (defined as the zero phase reference). By injecting $\tilde{I}$ with
various frequencies, the $|Z'(\omega)|$ and $\varphi_z(\omega)$ spectra are acquired, which is known to be a frequency-domain measurement. The non-zero negative $\varphi_z$ highlights the polarization effects that cause the voltage to lag the current. From measured $Z'$, $\sigma^*$ is obtained as,

$$\sigma^* = \frac{1}{\rho^*} = \frac{1}{KZ^*}, \quad (2.11)$$

where $K$ is the geometric factor (in m) of the measured sample that defines the proportionality between $\rho^*$ and $Z'$. For a cylinder sample (Figure 2.2a), $K$ is the base area divided by the sample length between electrodes M and N. In practice, $K$ is more accurately acquired by fitting a series of $|\rho^*|$ and $|Z'|$ measured on aqueous solutions with various known conductivities. In laboratory SIP measurements, 1D electric current flows through the sample and thus $\sigma^*$ represents the intrinsic electrical response assuming the sample is homogeneous at the measurement scale.

![Figure 2.2 Illustration of SIP measurement principles.](image)

Figure 2.2 Illustration of SIP measurement principles. (a) Laboratory SIP measurement set-up. (b) Determination of impedance from sinusoidal voltage and current signals.
As the phase responses of natural Earth materials containing no or small amount of electronically conducting minerals are small (e.g., less than 1 mrad to tens of mrad), accurate SIP measurements require a high-quality measurement device and a well-designed sample holder. The SIP device accuracy should be examined using a well-defined electric circuit comprised of high precision electronic parts (e.g., resistors and capacitors). The potential electrodes are built by placing a metallic electrode in a segment of electrolyte contacted with the sample (Figure 2.2a). This design avoids the intrusion of the metallic electrode into the sample that will result in high measurement errors due to the electrode polarization (Ulrich & Slater 2004). Zimmermann et al. (2008) presented a comprehensive study on the design of high accuracy SIP device and sample holder, where suggestions on the sample holder dimensions and current/potential electrode materials were provided. In general, the measurement accuracy of the whole SIP set-up can be evaluated by making measurements on aqueous solutions whose theoretical phase responses can be calculated. With an optimized SIP set-up, accurate phase data with errors less than 1 mrad can be readily acquired at low frequencies <100 Hz, whereas extra correction procedures may be needed for accurate high frequency (>100 Hz) data acquisition (Chapter 3).

While Figure 2.2a presents a specific sample holder design, other designs sharing the same measurement principle have been reported for different purposes. For example, in studies using SIP to monitor biogeochemical processes, ports are added for injecting reaction solutions/microbes and sampling pore fluid for analysis (Placencia-Gómez et al. 2013). More than one pair of potential electrodes may be installed to monitor different zones of the sample to understand the spatial variations of biogeochemical processes (Personna et
al. 2008, Zhang et al. 2012). To acquire the SIP data of consolidated rock samples, a different sample holder design with the rock core held between two end caps is needed to overcome the contact issues between electrodes and a hard surface (Binley et al. 2005, Kemna et al. 2012).

Although laboratory complex conductivity data are mostly collected from frequency-domain measurements, they are sometimes evaluated based on time-domain measurements (Gurin et al. 2013). In a time-domain measurement, a unidirectional current is driven between the current electrodes for a period of time and then abruptly switched off. The voltage recorded right before switching off the current is used to obtain the resistance (similar to \(|Z^*|\)). After switching off the current, the voltage drops suddenly to a secondary voltage, which then decays with time. This voltage decay curve (i.e., the voltage does not reduce to zero immediately) indicates the polarization effects in a time-domain form that is quantified by an integral parameter chargeability (S. Ward 1988, Binley 2015). Based on the proportionality between phase and chargeability, the complex conductivity parameters can be obtained (Lesmes & Frye 2001). Moreover, processing the voltage decay curve may reveal spectral electrical responses comparable to the frequency domain SIP (Tarasov & Titov 2007, Gurin et al. 2013).

2.3.2 Field measurements

Field surface SIP measurement shares the same four-electrode principle as laboratory measurement but has different electrode configurations (Figure 2.3). Field SIP has \(|Z^*|\) and
φ_z as the measured parameters based on Eq. (2.10). Assuming hemi-spherical current flow from point sources, the geometric factor \( K' \) (in m) for the electrode layout in Figure 2.3 is,

\[
K' = \frac{2\pi}{\left( \frac{1}{r_{AM}} - \frac{1}{r_{BM}} - \frac{1}{r_{AN}} + \frac{1}{r_{BN}} \right)},
\]

(2.12)

where \( r_x \) is the distance between the corresponding current and potential electrode. For a homogeneous subsurface, \( \sigma^* \) is obtained as \( 1/(K'Z^*) \), the same way as Eq. (2.11). However, for a heterogeneous subsurface, measured \( \sigma^* \) does not represent the intrinsic electrical response but instead is defined as an apparent complex conductivity that represents the electrical response from an equivalent homogeneous, isotropic half-space (Kemna 2000, Binley 2015). Acquiring the intrinsic spatial variations of \( \sigma^* \) in the subsurface requires inversion using a set of measurements from multiple four-electrode arrays (Kemna 2000).

In practice, raw data are preprocessed prior to the inversion to filter out abnormal responses (e.g., too high signals) from measurement errors. Positive \( \phi_z \) signals (i.e., positive apparent phase) are often considered as erroneous data as Earth materials should always exhibit a negative intrinsic phase due to their lossy electrical capacitance. However, error-free positive \( \phi_z \) can occur over heterogeneous media as demonstrated in Chapter 4 (Wang et al. 2021a). Discarding these positive \( \phi_z \) data will result in incorrect imaging and interpretation of the subsurface.

In field applications, it is not uncommon to extract complex conductivity information from time-domain measurements due to the shorter data acquisition time compared to the frequency-domain measurements (Flores Orozco et al. 2015, Saneiyan et al. 2019). In addition, there are increasing interests in extracting spectral electrical information from
field acquired time-domain decay curves (Fiandaca et al. 2013, Madsen et al. 2020). Although time-domain and frequency-domain measurements show comparable results (Maurya et al. 2018), acquiring high quality time-domain spectral data is still challenging and requires extra effort in the data processing.

![Diagram of field surface SIP measurements.](image)

Figure 2.3 Illustration of field surface SIP measurements.

### 2.4 SIP in environmental science

As an emerging geophysical technique in environmental science, SIP has drawn increasing attention to the non-invasive characterization and monitoring of contamination and various biogeochemical processes. Metallic wastes such as mine tailings and abandoned metals generally show high polarization strength, which is readily sensed by SIP (Gazoty et al. 2012, Placencia-Gómez et al. 2015). Non-aqueous phase liquid (NAPL) contaminants (e.g., oils) in porous media also show detectable SIP features as they act as electrically insulating phase (Vinegar & Waxman 1984, Vanhala 1997, Deng et al. 2018). Contamination of NAPL reduces the saturation degree with aqueous fluids, which results in reduced
imaginary conductivity (Schmutz et al. 2010, Shefer et al. 2013, Deng et al. 2018). However, more studies are needed to fully understand how NAPLs change the electrical properties of subsurface. Different from NAPL contaminants, aqueous contaminants (e.g., landfill leachates, saltwater) increase water saturation and/or the pore fluid conductivity by introducing fluids with excessive dissolved ions. These contaminants thereby show high real or DC conductivity features that are frequently sensed by DC electrical method, although it is challenging to distinguish them from high conductivity features potentially resulting from clay minerals. SIP (or IP) surveys additionally identify high clay content zones exhibiting high imaginary conductivity, which improve the interpretation of contamination patterns.

Another important component of SIP application is to monitor the biogeochemical processes by sensing the products and/or structural variations due to the mineralization and microbial activity (Davis et al. 2006, Slater et al. 2007). Microbial induced sulfide precipitation was found to exhibit distinct polarization signatures, making SIP a promising tool to monitor the bioremediation process that promotes sulfate reduction (Ntarlagiannis et al. 2005, Williams et al. 2005). Williams et al., (2009) demonstrated in the field scale that stimulated bioremediation produces iron sulfides, which enhance the IP signals, but not change the resistivity signal significantly. Flores Orozco et al., (2011) obtained similar IP signals in a long-term monitoring of the bioremediation of uranium at the same site. Calcite precipitation shows enhanced imaginary conductivity, which is efficiently sensed by SIP measurements (Izumoto et al. 2020, Saneiyan et al. 2020). Inspired by SIP sensing of these intentionally enhanced biogeochemical processes, people started to explore the
potentials of SIP to monitor the biogeochemical hotspots that have uncommonly high chemical reactivity and influence on ecosystems (McClain et al. 2003). Wainwright et al., (2016) proposed a Bayesian hierarchical method to integrate geochemical and IP data to estimate the presence probability of naturally reduced zones (hot spots for nitrogen loss) over the floodplain. Flores Orozco et al., (2020) identified biogeochemically active areas as high polarization zones in a municipal solid wastes landfill. Anoxic groundwater discharge zones in river corridors are also important biogeochemical hot spots due to the distinct redox gradient and precipitation of nanoparticle metal oxides. SIP can be potentially applied to identify these zones by mapping high surface area metal oxides, which will be discussed in Chapter 5 (Wang et al. 2021b).
Chapter 3 Extending Accurate Spectral Induced Polarization Measurements into the kHz Range: Modeling and Removal of Errors from Interactions between the Parasitic Capacitive Coupling and the Sample Holder

Abstract

Spectral induced polarization (SIP), describing the measurement of the frequency domain electrical impedance magnitude and phase of porous materials, has been widely used to characterize subsurface hydrological/biogeochemical properties and processes. SIP data collected at frequencies higher than 100 Hz are expected to describe the polarization of small particles providing insights into the physicochemical properties of clays, nanoparticles and microorganisms. However, the phase measurements at these high frequencies are often contaminated by errors due to the parasitic capacitive coupling of the SIP instrument, especially for lower conductivity samples. We developed a model showing the measured phase is the sum of the true sample phase and an error term $\omega C_{in} Z_s$, where $\omega$ is the angular frequency; $C_{in}$ is the instrument input capacitance and $Z_s$ is a measurable impedance function related to the sample holder properties and reference resistor. Based on this model, a new phase correction method is proposed that results in highly accurate SIP data up to 20 kHz as well as the determination of $C_{in}$. We tested the correction method using electric circuits, NaCl fluids and three unconsolidated samples (sand, sand-clay and

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sand-pyrite mixtures). The corrected phase for the circuit and NaCl fluid experiments showed excellent agreement with the theoretical phase response across the studied frequency range (errors <1 mrad). For unconsolidated samples, removal of errors results in phase spectra more consistent with expected polarization mechanisms, as based on phase peaks recorded for small pyrite and clay particles at high frequencies. These phase peaks could not be identified in the uncorrected data. Our approach can substantially enhance the value of the SIP method for the characterization of fine-grained sediments and rocks.

3.1 Introduction

Spectral induced polarization (SIP) is an emerging geophysical method that measures the complex conductivity/resistivity of porous materials from several mHz to tens of kHz. The method has been used to improve understanding of the electrical properties of porous materials by exploiting the sensitivity of complex conductivity to pore structure and biogeochemical processes (Kemna et al. 2012). This makes SIP valuable in a wide range of non-invasive subsurface characterization investigations, e.g., mapping metallic materials (e.g., Pelton et al. 1978) or contaminants (e.g., Vanhala 1997; Deng et al. 2018), monitoring remediation (e.g., Flores Orozco et al. 2015) and bacteria activity (e.g., Revil et al. 2012; Mellage et al. 2018).

The two parameters acquired from SIP measurements are impedance magnitude and phase in the frequency domain. One challenge of laboratory SIP measurements is the accuracy of the phase measurement as geophysical materials normally have low phase response (from less than 1 mrad up to tens of mrad). With modern instruments and well-designed sample
holders, it is practical to acquire accurate phase spectra below 100 Hz (referred to as ‘low
frequency (LF)’ in this paper) with less than 0.1 mrad errors (e.g., Zimmermann et al. 2008).
However, at frequencies higher than 100 Hz (referred to as ‘high frequency (HF)’ in this
paper), significant phase errors due to the unintended capacitive effects among electronic
components within the instrument, commonly called parasitic capacitive coupling (PCC),
have been observed by numerous studies (e.g., Slater & Lesmes 2002; Binley et al. 2005;
Kemna et al. 2012). These effects make the reliability of the measurements published in
some SIP studies uncertain at HFs.

Many studies have modeled or interpreted HF SIP data in order to extend the information
on polarization mechanisms to smaller time scales. Leroy et al. (2008) established a
mechanistic model to describe and predict both LF and HF polarization of porous materials
and compared the model against measurements made on glass beads. Kremer et al. (2016a)
applied HF SIP data to identify CO$_2$ dissolutions processes. Although both studies
attributed the HF phase response to the sample properties, they also recognized the
possibility that phase errors resulting from the instrumentation adversely impacted the data.
Such studies highlight the need to extend accurate phase measurements to HFs by careful
quantification and removal of errors.

Accurate SIP measurements require the quantitative analysis of phase errors resulting from
both the instrument and the sample holders. Some studies have reported SIP
instrumentation phase measurement accuracies of 1 mrad or even lower across both the LF
and HF range (e.g., Olhoeft 1985; Zimmermann et al. 2008; Abdulsamad et al. 2016).
However, when those instruments were applied to acquire the phase spectra of aqueous solutions for which the theoretical phase can be computed, abnormal responses were observed at HFs, especially for lower conductivity fluids. This observation indicates that, although the instrument records the phase accurately, the measured phase at HFs contains errors from the interaction between the PCC and the sample holder. Although PCC has been considered as a source of error in numerous previous publications, very few studies have investigated this phenomenon quantitatively. Ingeman-Nielsen (2006) developed an equivalent circuit model to describe the contact resistance and capacitive coupling in a field SIP survey and observed that increasing the frequency, dipole size, contact resistance or wire-to-ground capacitance increases the phase errors. At the lab scale, Zimmermann et al. (2008) proposed an electric circuit model to simulate a four-electrode sample holder connected to the instrument. Their model showed that the reference resistor as well as the impedance from the sample volume between the negative potential electrode and the negative current electrode results in current measurement errors, while the impedance from the potential electrodes causes the voltage measurement errors. Based on this model, they proposed a correction method to improve the accuracy of current measurements. Later, Huisman et al. (2016) proposed a correction method to remove the voltage measurement errors by measuring the electrode impedance. They acquired improved phase spectra up to 10 kHz for both NaCl fluids and unconsolidated samples. However, limitations to these correction methods remain including: 1) The correction relies on the acquisition of absolute voltage at each potential electrode and cannot be applied to a measurement system using differential amplifiers that record voltage difference only (such differential amplifiers are used in commercially marketed SIP instrumentation). Although Huisman et al. (2016)
provided a simplified correction equation for differential voltage measurement, it is only applicable when the two potential electrode impedances are identical, which is difficult to realize in real measurements. 2) The correction relies on the input capacitance of the instrumentation, which is an estimated parameter representing the strength of the PCC. As input capacitance varies among different SIP instruments and varies with environmental conditions, a reliable way to measure it is needed to maximize the accuracy of HF SIP measurements.

In this study, we present a new model that accurately predicts the HF phase errors caused by interactions between the instrument PCC and the sample holder. A new phase correction method is proposed based on this model that can be applied to the SIP instrument recording the absolute voltage at each electrode or the voltage difference between electrodes (more common) demonstrated here. This correction method includes a calibration of input capacitance for each measurement to increase the accuracy of the corrected phase. First, we present a detailed derivation of the phase error model and describe the phase correction method based on this model. Second, we verify the phase error model and correction method using well-defined electric circuits and NaCl fluids with a known phase response. Third, we compare the corrected and uncorrected phase results for three types of unconsolidated samples. Finally, we discuss the significance of the two key parameters involved in the proposed correction method and compared the correction with phase data collected above the SIP frequency range using a two-electrode method commonly referred to as dielectric spectroscopy or impedance spectroscopy (Kremer et al. 2016b).
3.2 SIP phase error model and correction

3.2.1 Principle of SIP measurements

The principle of the four-electrode SIP measurement is illustrated in Figure 3.1a. Sinusoidal voltages of various frequencies are applied to the sample between two current electrodes (A and B), while the voltage drops through a segment of the sample are recorded via two potential electrodes (M and N). To avoid electrode polarization at the potential electrodes, the metal part of the potential electrode is usually placed in a chamber filled with electrolyte so that the metal does not obtrude into the targeted sample (Vanhala & Soininen 1995). Non-polarizable porous materials are used to separate the electrolyte in the potential electrode chamber from the sample material packed into the main body of the sample holder. The electrical potentials inside the packed sample (i.e., $U_{s,p}$, $U_{s,n}$ and $\Delta U_s = U_{s,p} - U_{s,n}$) are transmitted to the amplifier (recorded as $U_{m,p}$, $U_{m,n}$ and $\Delta U_m = U_{m,p} - U_{m,n}$) via the electrolyte, metal electrode and connection cables. Current is determined by measuring the voltage drop ($\Delta U_{\text{ref}}$) across a reference resistor ($R_{\text{ref}}$) in series with the sample and obtained as $\Delta U_{\text{ref}}/R_{\text{ref}}$. Ideally, all the stimulus currents pass through the sample and reference resistor without leaking to either amplifier or ground (i.e., $I_1' = I_2' = I_3' = I_4' = 0$). This basic assumption indicates that 1) the current through the sample ($I_s$) is equal to that measured through the reference resistor ($I_m$) and 2) voltages recorded by the amplifier are equal to that inside the sample as no voltage drop occurs along the potential electrodes (i.e. $U_{s,p} = U_{m,p}$, $U_{s,n} = U_{m,n}$ and $\Delta U_s = \Delta U_m$). According to Ohm’s law, the sample impedance ($Z_s$) is equal to $\Delta U_s/I_s$, which is equal to the measured impedance ($Z_m$) in theory,

$$Z_s = |Z_s|e^{\phi_s} = \frac{\Delta U_s}{I_s} = \frac{\Delta U_m}{I_m} = |Z_m|e^{\phi_m} = Z_m,$$

(3.1)
where $|Z_s|$ is the sample complex impedance magnitude and $\phi_s$ is the sample phase; $|Z_m|$ is the measured complex impedance magnitude and $\phi_m$ is the measured phase.

Figure 3.1 Principle of SIP measurements. (a). Illustration of four-electrode sample holder (in black) connected to an SIP measurement system (in blue); (b). Equivalent electric circuit model of the sample holder (in black) and the SIP measurement system (in blue).
In SIP, the complex sample impedance is attributed to a number of mechanisms. Kemna *et al*. (2012) summarized various mechanisms and divided them into two categories: 1) electrochemical (EC) polarization due to the migration of charge carriers along the surface of porous material and 2) interfacial or Maxwell-Wagner (MW) polarization due to the charge accumulation at the interface between two phases with different dielectric permittivity and electrical conductivity. EC polarization (including membrane, electrical double layer and electrode polarization) describes the large relaxations occurring at LFs while MW polarization explains the dielectric behavior of multiphase system at HFs. Although this study focuses on the phase measurement accuracy, we will briefly discuss the polarization mechanisms to show the improvement of data interpretation after removing phase errors.

### 3.2.2 Electric circuit model with PCC

In the SIP instrument, the proximity of electronic components and wires results in numerous unintended capacitive effects, referred to here as PCC. These PCC effects create pathways that allow leakage currents to flow from high potential points to low potential points (e.g., chassis or ground) as described for field IP instrumentation by Dahlin & Leroux (2012). To explicitly show the effects, a single virtual capacitor connecting each amplifier input lead to ground is used to represent the complicated PCC effects (Figure 3.1a) (Huisman *et al*. 2016). Each virtual capacitor is assumed to have an identical capacitance, namely apparent input capacitance ($C_{in}$). For a well-designed instrument, $C_{in}$ is a very small quantity that is normally less than 10 pF (e.g., 4.7 pF in Huisman *et al*. 2016 and 8.9 pF for the instrument used in this study). However, the addition of these small
capacitors into the system will violate Eq. (3.1) and cause significant errors in phase measurements at HFs.

To quantitatively assess the PCC on SIP measurements, an equivalent linear electric circuit model is established in Figure 3.1b in a similar manner as Zimmermann et al. (2008) and Huisman et al. (2016). The circuit model simulates the sample holder as five connected impedance components: 1) $Z_s$ is the impedance of the sample packed between M and N and represents the targeted sample impedance to be measured; 2) $Z_{s,p}$ is the impedance of the sample material packed above $Z_s$ plus the contact impedance (i.e., impedance due to the current transfer from the electrolytic pore fluid of sample to the metal electrode) of the current electrode A; 3) $Z_{s,n}$ is the impedance of the sample packed below $Z_s$ plus the contact impedance of the current electrode B; 4) $Z_{e,p}$ is the electrode impedance of the positive potential electrode M and 5) $Z_{e,n}$ is the electrode impedance of the negative potential electrode N. According to the description in Section 3.2.1 and Figure 3.1a, electrode impedance summarizes the impedance from the sample/electrolyte interface to the metal electrode, the main components being the electrolyte impedance and the contact impedance at the electrolyte/metal interface. In the case of the circuit model, the leakage current $I_1'$, $I_2'$ and $I_3'$ pathways are modified to end at the negative port of stimulus voltage, which is equivalent to the zero potential ground. Also, $I_4'$ is short circuited by the wire and does not exist in the circuit model. The impedance of each virtual capacitor $Z_c$ has the expression,

$$Z_c = -\frac{1}{\omega C_{in}}i,$$

where $\omega$ is the angular frequency and equals $2\pi$ times frequency; $i$ is the imaginary unit where $i^2 = -1$. 
The proposed circuit model assumes that 1) the amplifier has an input impedance higher than 1 GΩ and is assumed to be an open circuit (dashed line in Figure 3.1b); 2) the amplifiers record voltages accurately; 3) the reference resistor is a perfect resistor and 4) connecting cables and wires have zero impedance. The assumptions point out that we only focus on the measurement errors due to the instrument PCC in this study and errors caused by other factors are considered negligible for our measurement system.

3.2.3 Derivation of phase error model

The proposed circuit model shows that $I_s \neq I_m$ due to the existence of $I'_{2}$ and $I'_{3}$. Besides, $U_{s,p} \neq U_{m,p}, U_{s,n} \neq U_{m,n}$ due to the voltage drops through $Z_{e,p}$ and $Z_{e,n}$ caused by $I'_{1}$ and $I'_{2}$. As Eq. (3.1) is not valid as a result of the PCC, a new relationship between $Z_s$ and $Z_m$ is derived as below.

3.2.3.1 Current measurement errors

According to the current divider rule, the relationship between $I_m$ and $I_s$ can be established from Figure 3.1b as (Zimmermann et al. 2008),

$$I_s = I_m \frac{R_{ref} + Z_c Z_{e,n} + Z_c + Z_{s,n} + Z_c||R_{ref}}{Z_{e,n} + Z_c},$$  

(3.3)

where $Z_c||R_{ref}$ represents the impedance of $Z_c$ and $R_{ref}$ in parallel,

$$Z_c||R_{ref} = \frac{R_{ref}Z_c}{R_{ref} + Z_c}. $$  

(3.4)

Substituting Eq. (3.2) and (3.4) into Eq. (3.3),
\[ I_s = I_m \frac{1 - R_{ref}(Z_{c,n} + Z_{s,n})\omega^2C_{in}^2 + (Z_{c,n} + Z_{s,n} + 2R_{ref})\omega C_{in}i}{1 + Z_{c,n}\omega C_{in}i} . \]  
\quad (3.5)

For an impedance \( Z \) with magnitude \(|Z|\) and phase \( \phi \), when \(-0.1 < \phi < 0\) and \( \omega C_{in}|Z|<0.2 \), we obtain the following approximations,

\[ Z = |Z| \cos \phi + |Z| \sin \phi i \approx |Z| + |Z|\phi i , \quad (3.6) \]

and

\[ 1 + \omega C_{in}Zi \approx 1 + \omega C_{in}|Z|i = \sqrt{1 + \omega^2 C_{in}^2 |Z|^2 e^{\tan^{-1}(\omega C_{in}|Z|)i}} \]
\[ \approx e^{\omega C_{in}|Z|i} . \]
\quad (3.7)

In addition, the real and imaginary part of the second order term \( \omega^2C_{in}^2Z^2 \) are negligible compared to that of \( 1+\omega C_{in}Zi \). Thus, when \( \omega C_{in}(|Z_{c,n}|+|Z_{s,n}|+2R_{ref})<0.2 \), and each impedance term has a phase less than 100 mrad, Eq. (3.5) can be simplified to,

\[ I_s = I_m e^{\omega C_{in}(|Z_{s,n}|+2R_{ref})i} , \quad (3.8) \]

which indicates that the PCC has insignificant impact on the amplitude of the current measurement, but introduces a non-negligible phase error that is proportional to \( \omega, C_{in} \) and \((|Z_{s,n}|+2R_{ref})\).

3.2.3.2 Voltage measurement errors

According to the voltage divider rule, the relationships between measured voltages and sample voltages are established as (Zimmermann et al. 2008),

\[ \frac{U_{m,p}}{U_{s,p}} = \frac{Z_c}{Z_{c,p} + Z_c} , \quad (3.9) \]
\[ \frac{U_{m,n}}{U_{s,n}} = \frac{Z_c}{Z_{c,n} + Z_c} . \quad (3.10) \]

With \( \Delta U_s = U_{s,p} - U_{s,n} \), \( \Delta U_m = U_{m,p} - U_{m,n} \), Eq.(3.9) and (3.10) can be combined into,
\[ \Delta U_s = \Delta U_m \left\{ 1 + \omega C_{in} \left[ Z_{c,p} + \left( Z_{c,p} - Z_{c,n} \right) \frac{U_{m,n}}{\Delta U_m} \right] i \right\}. \tag{3.11} \]

To simplify the expression of Eq. (3.11), we only consider the magnitude of each term as previously justified in Section 3.2.3.1. Also, we assume that the PCC has little impact on the amplitude of voltage measurements, which gives us \(|U_{m,n}|/|\Delta U_m| \approx (|Z_{s,n}|+R_{ref})/|Z_s|\). Eq. (3.11) is then simplified to,

\[ \Delta U_s = \Delta U_m \left\{ 1 + \omega C_{in} \left| Z_{c,p} \right| + \left( \left| Z_{c,p} \right| - \left| Z_{c,n} \right| \right) \frac{\left( |Z_{s,n}| + R_{ref} \right)}{|Z_s|} \right\} i. \tag{3.12} \]

Applying the approximation shown in Eq. (3.7), when the imaginary part of the expression inside \{ \} in Eq. (3.12) is less than 0.2, Eq. (3.12) is simplified to,

\[ \Delta U_s = \Delta U_m \omega C_{in} \left[ |Z_{c,p}| + (|Z_{c,p}| - |Z_{c,n}|) \frac{\left( |Z_{s,n}| + R_{ref} \right)}{|Z_s|} \right] i, \tag{3.13} \]

which indicates that the PCC has insignificant impact on the amplitude of the voltage measurement, but result in a phase error that is proportional to \( \omega \), \( C_{in} \) and an impedance function \(|Z_{c,p}|+(|Z_{c,p}|-|Z_{c,n}|)(|Z_{s,n}|+R_{ref})/|Z_s|\).

### 3.2.3.3 Impedance phase measurement errors

Dividing Eq. (3.13) by Eq. (3.8) provides the relationship between true sample impedance \( Z_s \) and measured impedance \( Z_m \) under the PCC effects,

\[ |Z_s| e^{\phi_s} = |Z_m| e^{\phi_m + \omega C_{in} \left( |Z_{c,p}| + (|Z_{c,p}| - |Z_{c,n}|) \frac{\left( |Z_{s,n}| + R_{ref} \right)}{|Z_s|} - |Z_{s,n}| - 2R_{ref} \right)} i. \tag{3.14} \]

Eq. (3.14) shows that the sample impedance magnitude is approximately the same as the measured value, whereas the sample phase is equal to the measured phase plus an error term. It should be noted that Eq. (3.14) is simplified from Eqs (3.5) and (3.11) using several approximations, and therefore is only valid under certain criteria as justified in Sections
3.2.3.1 and 3.2.3.2. In most cases, these criteria can be easily met by adjusting the sample holder appropriately as shown later in our experiments. By performing calculations on a wide range of synthetic circuits with predefined \( Z_s, Z_{s,n}, Z_{e,p} \) and \( Z_{e,n} \) and \( R_{ref} \), we have verified that Eq. (3.14) is able to predict \(|Z_m|\) and \( \phi_m \) with less than 5% errors from those predicted using original Eqs. (3.3) and (3.11) (See Appendix B for calculation details).

As convention in SIP measurements is to report the phase in impedance or complex resistivity space with a negative sign, we will present and discuss ‘−phase’ for the remainder of this paper. Rewriting the phase part of Eq. (3.14), we obtain the phase error model:

\[
-\phi_m(\omega) = \omega C_{in} Z_x + \left[ -\phi_s(\omega) \right],
\]

with

\[
Z_x = \left[ |Z_{e,p}| + (|Z_{e,p}| - |Z_{e,n}|) \frac{(|Z_{s,n}| + R_{ref})}{|Z_s|} \right] - \left( |Z_{s,n}| + 2R_{ref} \right).
\]

Eq. (3.15) shows that at each frequency, the measured phase \((-\phi_m)\) is the sum of the sample phase \((-\phi_s)\) and a phase error term \( \omega C_{in} Z_x \), where \( C_{in} \) is regarded as a constant related to the instrument properties and \( Z_x \) is an impedance term that is related to the impedance magnitude from various parts of the sample holder and the reference resistor as expressed in Eq. (3.16). As the impedance magnitude does not vary significantly at different frequencies, \( Z_x \) is treated as a frequency-independent parameter. Figure 3.2a shows simulated phase errors from 1 Hz to 20 kHz under different \( C_{in} \) and \( Z_x \) conditions. The phase errors range from 6 to 171 mrad at 20 kHz, 3 to 86 mrad at 10 kHz and 0.3 to 9 mrad at 1 kHz. Considering many studied materials are characterized by phase values from less than 1 mrad to tens of mrad, those errors will have significant impacts on \(-\phi_m\). The phase
errors decrease rapidly with decreasing frequencies. All the phase errors shown in Figure 3.2a become less than 1 mrad at 100 Hz and less than 0.1 mrad at 10 Hz. However, those errors will increase at all frequencies when $C_{in}$ and $Z_x$ are increased.

Figure 3.2 Examples of simulated phase errors using Eq. (3.15). (a). Phase errors under various $C_{in}$ and $Z_x$ conditions from 1 Hz to 20 kHz; (b). Impacts of various $Z_x$ on the measured phase spectra of a sample with constant phase 20 mrad ($C_{in} = 8.9 \, \text{pF}$).
3.2.3.4 Properties of $Z_x$

According to Eq. (3.16), $Z_x$ is a function of one known parameter $R_{\text{ref}}$ and four unknown parameters $|Z_s|$, $|Z_{s,n}|$, $|Z_{e,p}|$ and $|Z_{e,n}|$ that are mainly dependent on the sample holder geometry and the conductivity of packed materials. The component $Z_{s,p}$ does not appear in any equations (3.3) to (3.16), meaning it has no influence on the SIP measurement errors.

To better understand how each parameter influences $Z_x$, the 1st term $|Z_{e,p}|+(|Z_{e,p}|−|Z_{e,n}|)(|Z_{s,n}|+R_{\text{ref}})/|Z_s|$ in Eq. (3.16) is defined as an effective electrode impedance ($Z_e$), which can be considered as an electrode impedance basis $|Z_{e,p}|$ plus an extra impedance term contributed by the difference between $|Z_{e,p}|$ and $|Z_{e,n}|$. When $|Z_{e,p}|=|Z_{e,n}|$, $Z_e$ is simply equal to either electrode impedance without impedance difference effects, although this condition is difficult to realize in practice. When $|Z_{e,p}|>|Z_{e,n}|$, $Z_e$ has an impedance higher than $|Z_{e,p}|$ and vice versa. If $|Z_{e,p}|$ and $|Z_{e,n}|$ have too large a difference or $|Z_{s,n}|+R_{\text{ref}}$ is large relative to $|Z_s|$, $Z_e$ will be increased or decreased significantly on the basis of $|Z_{e,p}|$ and could become negative. Therefore, the value of $Z_x$ could be either positive or negative, depending on which term is larger, $Z_e$ or $|Z_{s,n}|+2R_{\text{ref}}$. According to the definition in Eq. (3.15), positive $Z_x$ (meaning positive phase error) will increase $-\phi_m$ (e.g., $Z_x=10$ and 40 kΩ in Figure 3.2b), while negative $Z_x$ (meaning negative phase error) will decrease $-\phi_m$ (e.g., $Z_x=-10$ kΩ in Figure 3.2b) and even make the polarity of $-\phi_m$ become negative i.e., measured raw phase is positive (e.g., $Z_x=-40$ kΩ in Figure 3.2b). This finding shows that the PCC could either increase or decrease $-\phi_m$ depending on the $Z_x$ value, which is determined by all five parameters in Eq. (3.16).
3.2.4 Phase correction method

According to the simplified phase error model shown in Eq. (3.15), $-\phi_m$ is linearly related to $Z_x$ with $\omega C_{\text{in}}$ as the slope and $-\phi_s$ as the intercept at each frequency. To determine $\omega C_{\text{in}}$ and $-\phi_s$ from the linear regression between $-\phi_m$ and $Z_x$, multiple $-\phi_m$ spectra collected at various $Z_x$ conditions for a packed sample are required. As described in Section 3.2.3.4, $Z_x$ is a dynamic parameter that can be varied significantly under different sample holder and reference resistor conditions. Here, we specifically consider one scenario with 1) $|Z_s|$, $|Z_{s,n}|$, $R_{\text{ref}}$ and $(|Z_{s,n}|+R_{\text{ref}})/|Z_s|$ being relatively small and 2) $|Z_{e,p}|$ and $|Z_{e,n}|$ being relatively large and similar, so that the electrode impedance will contribute primarily to $Z_x$ according to Eq. (3.16). By changing $|Z_{e,p}|$ and $|Z_{e,n}|$ simultaneously while keeping $|Z_s|$, $|Z_{s,n}|$, $R_{\text{ref}}$ unchanged, $Z_x$ will be changed which subsequently changes $-\phi_m$.

Figure 3.3 illustrates the principle of the proposed correction method. First, both potential electrodes of a packed sample are adjusted to have large and similar electrode length ($L_{el}$), i.e., the distance between sample/electrolyte interface and electrolyte/metal interface shown in Figure 3.3a. This will result in a relatively large $Z_x$ due to the large $|Z_{e,p}|$ and $|Z_{e,n}|$. To determine $Z_x$, three SIP measurements using different cable connections are conducted to acquire $|Z_s|$, $|Z_{s,n}|$, $|Z_{e,p}|$ and $|Z_{e,n}|$. $|Z_s|$ is simply acquired from the normal measurement with current injected from electrode A to B and voltage measured between M and N (Figure 3.3a1). This normal measurement also acquires $-\phi_m$, which is the measured phase requiring correction. $|Z_{s,n}|$ is measured from the modified normal measurement with the same current injection from A to B, but voltage measured between N and B (Figure 3.3a2). For $|Z_{e,p}|$ and $|Z_{e,n}|$, reciprocal measurements are applied as proposed by Huisman et al. (2016). Current
is injected between M and N, while voltage drops from M to A, and from B to N are measured to obtain $|Z_{e.p}|$ and $|Z_{e.n}|$, respectively (Figure 3.3a3). $Z_x$ can then be calculated with the measured $|Z_s|$, $|Z_{s,n}|$, $|Z_{e.p}|$ and $|Z_{e.n}|$ at a single frequency, as well as the known $R_{ref}$ using Eq. (3.16). The acquisition of $|Z_s|$, $|Z_{s,n}|$, $|Z_{e.p}|$ and $|Z_{e.n}|$ assumes that the measured impedance magnitude is approximately the same as the true magnitude as justified in Section 3.2.3.3. This first dataset is recorded as $-\phi_m^1$ at $Z_x^1$. Second, the $L_{el}$ of both potential electrodes for the same packed sample is reduced simultaneously and all the measurements mentioned above are repeated (Figure 3.3b). When the cross-sectional area, electrolyte conductivity and the metal electrode of the potential electrode stay the same, reducing $L_{el}$ will decrease the electrode impedance as well as $Z_x$. This second dataset is recorded as $-\phi_m^2$ at $Z_x^2$. The process continues by reducing $L_{el}$ and acquiring more datasets, e.g., $-\phi_m^3$ at $Z_x^3$, …, $-\phi_m^n$ at $Z_x^n$ (Figure 3.3c). At each frequency, the linear regression between $-\phi_m$ ($-\phi_m^1, -\phi_m^2, \ldots, -\phi_m^n$) and $Z_x$ ($Z_x^1, Z_x^2, \ldots, Z_x^n$) provides the corrected phase from the intercept and $C_{in}$ from the slope divided by $\omega$. 
a. Pack the sample and adjust both potential electrodes to have large electrode length ($L_{el}$). Acquire $-\phi_m$ and $|Z_s|$ from normal measurement (a1); acquire $|Z_{s,n}|$ from modified normal measurement (a2); acquire $|Z_{n,p}|$ and $|Z_{n,m}|$ from reciprocal measurement (a3). Calculate $Z_n$. This first dataset is recorded as $-\phi_m^1$ at $Z_X^1$.

![Flow chart illustrating the principle of the proposed phase correction method.](image)

b. Adjust both potential electrodes to reduce $L_{el}$. Repeat the three SIP measurements shown in a1, a2 and a3 and obtain the second dataset: $-\phi_m^2$ at $Z_X^2$.

c. Repeat step b to acquire more datasets: $-\phi_m^3$ at $Z_X^3$, ..., $-\phi_m^n$ at $Z_X^n$.

d. Solve the corrected phase and $C_{in}$ from linear regression between $-\phi_m$ and $Z_X$ at each frequency.

![Graph showing linear regression between phase and frequency.](image)

Figure 3.3 Flow chart illustrating the principle of the proposed phase correction method.
### 3.3 Electric circuit experiments

#### 3.3.1 SIP instrument accuracy

SIP data were collected using a portable SIP field/lab unit manufactured by Ontash & Erma, Inc. The instrument has the same measurement configuration as shown in Figure 3.1a. The stimulus voltages have an amplitude 1 V. Coaxial cables were used to connect samples with instrument ports. The instrument accuracy was examined by an electric circuit shown in Figure 3.4, where $Z_{e,p}$, $Z_{e,n}$, $Z_{s,p}$ and $Z_{s,n}$ had zero resistance, meaning no sample holder effects. $R_{\text{ref}}$ was set to be 100 Ω so that the resultant $Z_x$ was only 100 Ω, causing negligible errors according to Eqs (3.15) and (3.16). The test circuit for $Z_s$ was built as suggested by Vanhala & Soininen (1995) to simulate a soil sample that has two relaxations in the studied frequency. Figure 3.5 shows that our SIP instrument has high accuracy for both magnitude and phase measurements from 0.1 Hz to 20 kHz. The measurement errors for magnitude and phase are less than 0.5% and 1 mrad, respectively. The same results should be expected of other well-designed SIP instruments, i.e. the instrument itself is capable of recording accurate phase data in the absence of sample holder errors (when $Z_x \approx 0$).

![Electric circuit](image)

Figure 3.4 Electric circuit built using commercial high accuracy resistors and capacitors with known values. The model circuit representing the sample $Z_s$ was fixed while $Z_{e,p}$, $Z_{e,n}$, $Z_{s,p}$, $Z_{s,n}$ and $R_{\text{ref}}$ were varied for different tests. Stimulus voltages were applied via A and B, while voltage difference were measured between M and N as shown in Figure 3.1b.
Figure 3.5 SIP instrument accuracy for the model circuit when Figure 3.4 had $Z_{s,p} = Z_{s,n} = Z_{s,p} = Z_{s,n} = 0$ and $R_{ref} = 100 \ \Omega$. Solid line shows the calculated SIP response using the parameters in Figure 3.4 while black dots showed the measured response.

3.3.2 HF phase errors and correction

To simulate the samples packed in a sample holder, non-zero resistors were used for $Z_{s,p}$, $Z_{s,n}$, $Z_{e,p}$ and $Z_{e,n}$ shown in the circuit in Figure 3.4. Firstly, we tested the case where $Z_{s,p}$ and $Z_{s,n}$ were fixed to be 2 kΩ and $R_{ref}$ was set to be 1 kΩ. Five pairs of $Z_{e,p}$ and $Z_{e,n}$ with identical resistance 20, 40, 60, 80 and 100 kΩ were used, which resulted in the corresponding $Z_x$ values of 16, 36, 56, 76 and 96 kΩ. Under each $Z_x$ condition, SIP data were collected and compared with the calculated true phase of $Z_s$ circuit (Figure 3.6a). At frequencies below 100 Hz, all $-\phi_m$ show high agreement with the true phase with errors less than 1 mrad. The divergence among the phase curves starts to be observed at 100 Hz and, with the distance between the curves increasing significantly with increasing frequency. At each frequency above 100 Hz, $-\phi_m$ increases with increasing $Z_x$, although the targeted circuit $Z_s$ stays unchanged. At 20 kHz, $-\phi_m$ ranges from 28 to 104 mrad, which contains large errors from 16 to 91 mrad compared with the true phase of the simulated
sample \( Z_s \) (i.e., 12 mrad). At 10 kHz, the measured phase errors are reduced to the range 8 to 46 mrad, remaining significant as the true phase is only 20 mrad. At 1 kHz, the phase error at \( Z_x = 16 \, \text{k\Omega} \) is 0.8 mrad, whereas \( Z_x = 96 \, \text{k\Omega} \) still results in a 5 mrad error that need to be removed. The shapes of the \( -\phi_m \) spectra at HF's change dramatically under the influence of \( Z_x \) and cause the phase peak of \( Z_s \) to be unidentifiable. While \( -\phi_m \) shows significant errors at HF's, all the measured impedance magnitudes are close to the true magnitude with errors less than 0.5% (Figure 3.6c).

Figure 3.6 Phase correction for the model electric circuit \( Z_s \) shown in Figure 3.4 when \( Z_{s,0}=2 \, \text{k\Omega}, Z_{s,n}=2 \, \text{k\Omega} \) and \( R_{\text{ref}}=1 \, \text{k\Omega} \). (a) \( -\phi_m \) at various \( Z_x \) conditions (open circles) versus corrected phase (solid circles); (b) Examples of linear regression between \( -\phi_m \) and \( Z_x \) at 1, 5, 10 and 20 kHz; (c) Impedance magnitude measured at various \( Z_x \) conditions; (d) \( C_{\text{in}} \) determined from each \( -\phi_m \sim Z_x \) regression from 10 Hz to 20 kHz.
To obtain the corrected phase and $C_{in}$, linear regression between $-\phi_m$ and $Z_x$ at each frequency was conducted, with examples at 1, 5, 10 and 20 kHz shown in Figure 3.6b. The high $R^2$ values (>0.999) above 1 kHz indicate a strong linear relationship between $-\phi_m$ and $Z_x$, being consistent with Eq. (3.15). From each linear regression equation $y= ax+b$, the corrected phase at that frequency was obtained as the intercept $b$ and $C_{in}$ was obtained by dividing the slope $a$ by $\omega$ with proper unit conversions. Figure 3.6a shows that the corrected phase is similar to the true phase with errors less than 1 mrad. $C_{in}$ was determined to be 7.5 pF from 500 Hz to 20 kHz with less than 0.05 pF variation (Figure 3.6d). The dramatic change of $C_{in}$ and $R^2$ below 500 Hz is attributed to the poor linear regression when all $-\phi_m$ are similar to the true phase with small errors. As $C_{in}$ is a frequency independent parameter, the average value of $C_{in}$ obtained from 1 to 20 kHz where the linear regression is significant will be presented in all the results in this study.

In the first test mentioned above, the phase errors are mainly contributed by the electrode impedances $Z_{e,p}$ and $Z_{e,n}$. To demonstrate the impacts of $Z_{s,n}$ and $R_{ref}$, a second test was conducted by increasing $Z_{s,n}$ and $R_{ref}$ in the circuit of Figure 3.4 to 20 and 10 kΩ, respectively. Again, five SIP measurements were conducted with the same five pairs of $Z_{e,p}$ and $Z_{e,n}$, but lower $Z_x$ than the first test due to the increased $Z_{s,n}$ and $R_{ref}$ (Figure 3.7). The phase errors are observed as expected at HFs, but with different values from Figure 3.6a. At $Z_{e,p}/Z_{e,n}=20$ kΩ, $-\phi_m$ above 1 kHz is less than the true phase and even becomes negative at 16 and 20 kHz due to the negative $Z_x$. When $Z_{e,p}/Z_{e,n}=40$ kΩ, the resultant $Z_x$ becomes zero, making $-\phi_m$ spectra similar to the calculated curve with errors less than 1 mrad. This observation is attributed to the fact that zero $Z_x$ means $-\phi_m$ is unaffected by the PCC and
should contain no phase errors according to Eq. (3.15). In general, at the same $Z_{e,p}/Z_{e,n}$ condition, $-\phi_m$ at each frequency in Figure 3.7 has less error than observed in Figure 3.6 due to the reduced $Z_x$ caused by increased $Z_{s,n}$ and $R_{ref}$ value. The same correction procedures were applied to the second test and the corrected phase again show excellent match with the calculated curve (errors less than 1 mrad). $C_{in}$ was determined to be 9.4 pF, which is slightly higher than that obtained from the first test. We will discuss the variations of $C_{in}$ later in Section 3.6.2. The two circuit experiments show that $-\phi_m$ at HFs are linearly dependent on $Z_x$ as predicted by Eq. (3.15). The proposed phase correction method reduces the errors below 1 mrad and meanwhile provides a promising way to obtain the $C_{in}$ of the SIP instrument.

![Figure 3.7](image)

Figure 3.7 Phase correction for the model electric circuit $Z_s$ shown in Figure 3.4 when $Z_{s,p}=2$ k$\Omega$, $Z_{s,n}=20$ k$\Omega$ and $R_{ref}=10$ k$\Omega$. (a) $-\phi_m$ at various $Z_x$ conditions (open circles) versus corrected phase (solid circles); (b) Examples of linear regression between $-\phi_m$ and $Z_x$ at 1, 5, 10 and 20 kHz.

### 3.4 Lab column experiments

#### 3.4.1 Sample preparation

Fluid/unconsolidated samples were packed into an acrylic cylinder sample holder with 2.4 cm inner diameter and 9.3 cm height to conduct SIP measurements (Figure 3.1a). Ag-AgCl
wires were prepared by soaking clean silver wire (99.99% Ag, 2.05 mm diameter) in bleach for 30 min. Coiled Ag-AgCl wires were installed at the top and bottom end caps as two current electrodes. Two clear carbonate tubes with inner diameter 3.2 mm were used as the chamber of potential electrodes and were placed at 3.1 cm and 6.2 cm away from the top of sample holder. Straight Ag-AgCl wires encased in threaded housing were mated to a threaded nut attached on the electrode chamber so that $L_{el}$ could be adjusted to produce various electrode impedances. Small amounts of non-polarizable cotton were used to separate the unconsolidated samples from the electrolyte filled in the potential electrode chamber.

NaCl fluids with 0.01 or 0.1 S/m conductivity were used to saturate unconsolidated samples. Clean Ottawa sand (0.50-0.75 mm) was used for preparation of various unconsolidated samples. The sand was washed and soaked in deionized water for 24 hours to remove ions attached on the grain surface. For unconsolidated sample packing, all the samples were first saturated by the fluids with desired conductivity in the beaker and then packed into the sample holder. The packing was conducted on a shaker to remove any air bubbles and promote a uniform packing. All the unconsolidated samples were considered to be fully saturated. The same saturating fluid was also used as the electrolyte filling the potential electrode chamber. The electrolyte conductivity was assumed to be the same as sample pore fluid conductivity after equilibrium. All the SIP measurements were conducted at a room temperature of 20±1°C.
3.4.2 Phase correction

The phase corrections on various samples were performed based on the procedures described in Section 3.2.4. For each sample, five SIP datasets were collected under five $Z_x$ conditions by adjusting $L_{el}$ of $|Z_{e,p}|$ and $|Z_{e,n}|$ simultaneously. To avoid overly high or low $Z_e$ according to Eq. (3.16) and Section 3.2.3.4, $|Z_{e,p}|$ and $|Z_{e,n}|$ were kept as close as possible (<5 kΩ difference) and $R_{ref}$ was always smaller than $|Z_s|$ so that $(|Z_{e,p}|-|Z_{e,n}|)(|Z_{s,n}|+R_{ref})/|Z_s|$ is small. Throughout all the measurements, $Z_e$ was close to $|Z_{e,p}|$ and was higher than $|Z_{s,n}|+2R_{ref}$, resulting in larger $-\phi_m$ compared to the expected sample phase as discussed in Section 3.2.3.4. As the measured $|Z_{e,p}|$, $|Z_{e,n}|$, $|Z_{s,n}|$ and $|Z_s|$ had variations less than 0.5% at frequencies from 100 Hz to 20 kHz, their values at 1 kHz were used to calculate $Z_x$.

NaCl fluid was used to examine the phase correction performance as its theoretical phase response is well documented as (Vanhala & Soininen 1995):

$$\phi = \tan^{-1}\left(\frac{\omega\varepsilon_0\varepsilon_r}{\sigma'}\right), \quad (3.17)$$

where $\sigma'$ is the NaCl fluid conductivity; $\varepsilon_0$ is the vacuum permittivity ($8.85\times10^{-12}$ F/m) and $\varepsilon_r$ is the dielectric constant of water, which is 80 at 20 °C (Malmberg & Maryott 1956).

3.5 Results

3.5.1 Phase correction for NaCl fluids

The $-\phi_m$ spectra of the 0.01 S/m NaCl fluids under five $Z_x$ conditions are shown in the left panel of Figure 3.8a. At frequencies below 10 Hz, all $-\phi_m$ are less than 0.1 mrad, indicating a well-designed sample holder without issues causing LF phase errors. Starting from 100 Hz, the deviation of $-\phi_m$ from the theoretical curve is observed. The absolute phase errors
increase with both increasing frequency and $Z_x$, which is expected from Eq. (3.15). At 20 kHz, $-\phi_m$ ranges from 50 to 141 mrad, containing 41 to 132 mrad errors compared to the theoretical phase (i.e. 9 mrad). These errors correspond to relative errors as high as 456% to 1467%, which completely mask the true sample phase. At 10 kHz, the phase errors under the studied $Z_x$ conditions are reduced to the range from 21 to 66 mrad but are still much higher than the sample response (i.e. 4.5 mrad). Even at 1 kHz, unacceptable errors from 2 to 7 mrad can still be observed. When the frequencies drop below 100 Hz, all phase errors are reduced to be under 1 mrad. The results show that $-\phi_m$ at HFs is dominated by the phase errors, which are largely dependent on the sample holder property $Z_x$ instead of the targeted sample property. During all the SIP measurements shown in the left panel of Figure 3.8a, the packed fluid was stabilized and unchanged. However, simply adjusting $L_{el}$ resulted in completely different $-\phi_m$ spectra at HFs, which demonstrated that $-\phi_m$ contained errors in addition to the sample phase. Nevertheless, these errors are insignificant at LFs.
Figure 3.8 Phase correction for the NaCl fluids with different conductivity. (a). Conductivity of 0.01 S/m, |Z|=4.8 kΩ, |Z_{s,n}|=6.5 kΩ, R_{ref}=1 kΩ; (b). Conductivity of 0.1 S/m, |Z|=0.56 kΩ, |Z_{s,n}|=0.84 kΩ, R_{ref}=0.10 kΩ. For each sample, left panel: $-\phi_m$ at various Z_x conditions (open circles) versus corrected phase (solid circles); right panel: examples of linear regression between $-\phi_m$ and Z_x at 1, 5, 10 and 20 kHz.

To perform the phase correction, linear regressions between $-\phi_m$ and Z_x were established at each frequency (e.g., examples in the right panel of Figure 3.8a). Similar to the circuit experiments, strong linear relationships with $R^2>0.99$ between $-\phi_m$ and Z_x were obtained at HFs. The corrected phase obtained from the intercept of each linear equation shows excellent agreement with the theoretical curve with errors less than 1 mrad (red solid dots in the left panel of Figure 3.8a). To check the repeatability of the proposed phase correction
method, the entire procedure including both sample packing and correction was repeated
three times. The uncertainties of the corrected phase are within ±1 mrad at 20 kHz, ±0.5
mrad at 10 kHz and ±0.05 mrad at 1 kHz, which demonstrates that our correction method
produces consistent results.

For the 0.1 S/m NaCl fluid, \( -\phi_m \) shows a similar trend to that of the 0.01 S/m NaCl fluid,
but with reduced absolute phase errors (Figure 3.8b). The lower phase errors are attributed
to the reduced electrode impedance when higher conductivity fluid fills the potential
electrode chambers. Nevertheless, \( -\phi_m \) at HFs was still dominated by phase errors instead
of true sample phase. By performing the correction procedures, the phase errors were
successfully reduced to be less than 1 mrad. For both NaCl fluids experiments, the
instrument \( C_m \) was determined to be 8.6 pF, being slightly different from that obtained in
electric circuit experiments (i.e. 7.6 pF and 9.3 pF).

3.5.2 Phase correction for clean sand

The phase corrections for clean sands fully saturated with 0.01 or 0.1 S/m NaCl fluids are
shown in Figure 3.9. As expected, \( -\phi_m \) above 100 Hz is strongly affected by electrode
impedance as evident by changes in \( -\phi_m \) with changes in \( L_e \). Strong linear relationships
were established between \( -\phi_m \) and \( Z_x \) for both saturated sand samples, indicating that Eq.
(3.15) also works well for unconsolidated samples. The uncorrected phase spectra
overestimate the true phase response of the sample with unknown errors. For sand saturated
with 0.01 S/m fluid, the corrected phase at 20 kHz is only around 20 mrad, although \( -\phi_m \)
could be as high as 165 mrad when \( Z_x \) is 134 k\( \Omega \). Even at the lowest \( Z_x \) condition coinciding
with the shortest possible $L_{el}$ without the metal electrode entering the sample, $-\phi_m$ is 56 mrad, still much higher than the corrected phase. The corrected phase spectra show a significantly reduced phase, but with a similar shape compared to $-\phi_m$ spectra. For clean sand with little EC polarization occurring, the HF phase response is mainly due to MW polarization (Leroy et al. 2008). Using uncorrected $-\phi_m$ spectra for data interpretation will attribute the errors to the MW polarization and therefore overestimate the contribution from MW polarization.

Figure 3.9 Phase correction for the clean sands fully saturated by different NaCl fluids. (a). 0.01 S/m fluid, $|Z_s|=18$ kΩ, $|Z_{s,n}|=25$ kΩ, $R_{ref}=1.0$ kΩ; (b). 0.1 S/m fluid, $|Z_s|=2.3$ kΩ, $|Z_{s,n}|=3.2$ kΩ, $R_{ref}=1.0$ kΩ. For each sample, left panel: $-\phi_m$ at various $Z_x$ conditions (open circles) versus corrected phase (solid circles); right panel: examples of linear regression
between \(-\phi_m\) and \(Z_x\) at 1, 5, 10 and 20 kHz.

For sand saturated with 0.1 S/m fluid, the phase response resulting from MW polarization was expected to be decreased due to the increased bulk conductivity (Lesmes & Morgan 2001). No obvious phase increase at HFs is observed in the corrected phase spectra. At frequencies above 3 kHz, the phase is over corrected to be positive, which is not physically reasonable. As the corrected phase values only range from 0.05 to 1 mrad, this overcorrection might be attributed to the small uncertainty of the proposed correction method (e.g., \(\pm 1\) mrad at 20 kHz mentioned in Section 3.5.2). Although the corrected phase cannot be accurately determined as it is close to zero, it provides valuable information showing that the sand saturated with 0.1 S/m fluid has very weak polarization at HFs. In contrast, the uncorrected phase is misleading in suggesting that the sample polarizes significantly at HFs.

3.5.3 Phase correction for sand-pyrite mixtures

Sand-pyrite mixtures (1% pyrite by weight) were used to examine the correction performance on samples with relaxations occurring at HFs (Figure 3.10). From \(-\phi_m\) spectra, it can be roughly inferred that the relaxation time decreases with decreasing pyrite particle size and fluid resistivity, which is consistent with previous studies on the polarization of metallic materials at LFs (e.g., Pelton et al. 1978; Slater et al. 2005; Revil et al. 2015a). At HFs, \(-\phi_m\) spectra exhibit completely different shapes from the corrected ones. According to Revil et al. (2015b), the relaxation behavior of phase spectra is usually characterized by either a well-defined peak or a plateau. The \(-\phi_m\) spectra exhibit both types of behaviors for sample a, c and d, while the corrected phase spectra only show well-defined peaks. The
shapes of these $-\phi_m$ spectra are strongly impacted by $Z_x$ but approach the corrected spectra with decreasing $Z_x$. For sample b, as the phase peak appears at LFs, it is also well observed in each $-\phi_m$ spectrum due to the negligible phase errors. Although the influence of errors on the phase peak value of each sample is not significant in Figure 3.10, it could become significant when a peak occurs at an even higher frequency. The variations of the phase peak magnitudes among the four samples is attributed to variations in the packing of the samples as the phase magnitude (proportional to the chargeability) should only depend on the pyrite concentration (e.g., Wong 1979; Revil et al. 2015a).
a. Small-0.01 S/m

| $|Z_x|/|Z_{x,n}|/Z_4$ (kΩ) | 158 / 158 / 133 | 144 / 143 / 120 | 123 / 122 / 101 | 103 / 102 / 79 | 74 / 74 / 49 | Corrected |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|

-Phase (mrad) vs. Frequency (Hz)

b. Large-0.01 S/m

| $|Z_x|/|Z_{x,n}|/Z_4$ (kΩ) | 166 / 165 / 142 | 143 / 139 / 124 | 118 / 116 / 97 | 96 / 95 / 78 | 75 / 73 / 53 | Corrected |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|

-Phase (mrad) vs. Frequency (Hz)

c. Small-0.1 S/m

| $|Z_x|/|Z_{x,n}|/Z_4$ (kΩ) | 45 / 45 / 41 | 38 / 38 / 32 | 31 / 30 / 27 | 24 / 23 / 21 | 17 / 15 / 15 | Corrected |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|

-Phase (mrad) vs. Frequency (Hz)

d. Large-0.1 S/m

| $|Z_x|/|Z_{x,n}|/Z_4$ (kΩ) | 44 / 44 / 38 | 37 / 36 / 34 | 31 / 30 / 28 | 23 / 23 / 18 | 16 / 15 / 13 | Corrected |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|

-Phase (mrad) vs. Frequency (Hz)
Figure 3.10 Phase correction for the sand-pyrite mixtures fully saturated by 0.01 and 0.1 S/m NaCl fluids. Pyrites with two different particle size were used: small (0.125–0.25 mm) and large (0.25–0.5 mm). (a). \( |Z_s| = 17 \, \text{k}\Omega \), \( |Z_{s,n}| = 23 \, \text{k}\Omega \), \( R_{\text{ref}} = 1.0 \, \text{k}\Omega \); (b). \( |Z_s| = 16 \, \text{k}\Omega \), \( |Z_{s,n}| = 23 \, \text{k}\Omega \), \( R_{\text{ref}} = 1.0 \, \text{k}\Omega \); (c). \( |Z_s| = 22 \, \text{k}\Omega \), \( |Z_{s,n}| = 3.1 \, \text{k}\Omega \), \( R_{\text{ref}} = 1.0 \, \text{k}\Omega \); (d). \( |Z_s| = 2.2 \, \text{k}\Omega \), \( |Z_{s,n}| = 3.3 \, \text{k}\Omega \), \( R_{\text{ref}} = 1.0 \, \text{k}\Omega \). For each sample, left panel: \( -\phi_m \) at various \( Z_x \) conditions (open circles) versus corrected phase (solid circles); right panel: examples of linear regression between \( -\phi_m \) and \( Z_x \) at 1, 5, 10 and 20 kHz.

At frequencies above 1 kHz, the uncorrected \( -\phi_m \) spectra for all four samples have similar shapes showing consistent phase increases with increasing frequency. After correction, the HF parts of these spectra vary between samples saturated with different conductivity fluids. At 0.01 S/m, an increase of phase with increasing frequency is observed following the relaxation. This phase increase has a similar shape and strength to that observed for sand saturated by 0.01 S/m fluid. As the volume of pyrite was only 0.5% in the sand-pyrite mixtures, we expect the pyrite to have little effect on the HF MW polarization. As a result, both types of samples (i.e. sand and sand-pyrite) saturated with the same conductivity fluid should have similar phase response from MW polarization. However, the sand-pyrite mixtures have an EC polarization covering a broad frequency range, which also contributes to the HF phase response. When the saturating fluid conductivity increases to 0.1 S/m, the MW polarization produces a negligible phase response similar as that observed for clean sand in Figure 3.9b. Therefore, the corrected phase spectra of sand-pyrite mixtures c and d is dominated by the EC polarization even at HFs and does not exhibit the phase increase shown in samples a and b. Without correction, the phase response at HFs for sample c and d can easily be misinterpreted as a MW polarization effect.
3.5.4 Phase correction for sand-clay mixtures

The polarization of clay materials has been studied extensively at LFs (e.g., Vinegar & Waxman 1984; Slater et al. 2006). However, polarization measurements at HFs are challenging due to the difficulties in the acquisition of accurate phase data. The phase corrections performed on various fully saturated sand-clay mixtures are shown in Figure 3.11. At HFs, $-\phi_m$ increases sharply with increasing frequency, similar to other samples shown in the previous sections. After correction, the rate of phase increase with increasing frequency is reduced significantly. In general, the sand-clay mixtures show constant high phase at HFs, being different from that of sand and sand-pyrite. Considering the small particle size of clays, it is expected that the relaxation of sand-clay mixtures due to EC polarization mainly occurs at HFs. Two different types of clay exhibit distinct phase spectra. The increase in saturating fluid conductivity for the same type of clay reduces the phase strength but does not change the spectra shape significantly. The mechanisms of polarization will not be discussed in detail in this study as we focus more on the phase correction method. It is clear that the true response of the samples could not be identified using uncorrected phase data. The proposed phase correction method provides a more complete reliable phase spectrum to better study the polarization of clay materials.
Figure 3.11 Phase correction for sand-clay mixtures fully saturated by 0.01 and 0.1 S/m NaCl fluids. Two different types of clay were used: kaolin and bentonite. Clay content was 10% by weight. (a). $|Z| = 4.8 \, \text{k}\Omega$, $|Z_{s,n}| = 7.2 \, \text{k}\Omega$, $R_{\text{ref}} = 1.0 \, \text{k}\Omega$; (b). $|Z| = 1.9 \, \text{k}\Omega$, $|Z_{s,n}| = 2.9 \, \text{k}\Omega$, $R_{\text{ref}} = 1.0 \, \text{k}\Omega$; (c). $|Z| = 3.5 \, \text{k}\Omega$, $|Z_{s,n}| = 5.1 \, \text{k}\Omega$, $R_{\text{ref}} = 1.0 \, \text{k}\Omega$; (d). $|Z| = 1.8 \, \text{k}\Omega$, $|Z_{s,n}| = 2.5 \, \text{k}\Omega$, $R_{\text{ref}} = 1.0 \, \text{k}\Omega$. For each sample, left panel: $-\phi_m$ at various $Z_x$ conditions (open circles) versus corrected phase (solid circles); right panel: examples of linear regression between $-\phi_m$ and $Z_x$ at 1, 5, 10 and 20 kHz.

3.6 Discussion

3.6.1 Effects of $Z_x$ on $-\phi_m$

The proposed correction method was successfully applied to both fluids and a variety of unconsolidated samples. At HFs, $-\phi_m$ contains both true sample phase and significant phase errors. Our experiments show that for a packed sample, simply adjusting $L_{el}$ changes the electrode impedance, which subsequently changes $-\phi_m$ due to the changed $Z_x$. This observation alone indicates that using $-\phi_m$ without correction will result in misinterpretation of the sample electrical properties. For all the tested samples, $-\phi_m$ at HFs shows a very strong linear relationship with $Z_x$ ($R^2 > 0.99$), from which the corrected phase is obtained as the intercept representing no $Z_x$ effects. The results demonstrate that the derived phase error model (i.e., Eqs (3.15) and (3.16)) using the electrical circuit model accurately describe the PCC effects on $-\phi_m$.

Among the five variables determining $Z_x$ shown in Eq. (3.16), $|Z_{e,p}|$, $|Z_{e,n}|$, $|Z_{s,n}|$ and $|Z_s|$ are strongly dependent on the sample holder geometry and packed material conductivity, while $R_{\text{ref}}$ is selected by the user. As shown in the legend and caption from Figure 3.8 to Figure 3.11, the electrode impedance accounts for a much greater fraction of $Z_x$ than $|Z_{s,n}|$ and $R_{\text{ref}}$ throughout all the experiments in this study. The high electrode impedance is attributed to the small cross-sectional area (i.e., 8 mm²) of the electrode chamber and low conductivity.
of the filled electrolyte, e.g., 0.01 S/m electrolyte with only 10 mm length has an impedance as high as 125 kΩ. Although reduction of $L_{el}$ decreases the electrode impedance, too short a value of $L_{el}$ might cause additional errors due to the polarization of the metal electrode when proximal to the current flow vectors (Ulrich & Slater 2004). Therefore, the electrode impedance effects are unavoidable for samples saturated with low conductivity fluids if the same saturating fluid is used as the electrolyte as for the potential electrodes. When using potential electrodes filled with over saturated salt solution having very high conductivity (e.g. in Okay et al. 2014), the contribution of the electrode impedance to $Z_x$ and phase errors might become less important. In this case, $|Z_{x,n}|$ and $R_{ref}$ will dominate $Z_x$ and primarily account for the phase errors, which causes $-\phi$ less than the expected sample phase due to a negative $Z_x$. In addition, the exchange of ions between sample pore fluids and electrolyte driven by the concentration gradient could influence the sample conductivity significantly and introduce extra errors (Schmutz et al. 2010). It can be speculated that, when the conductivities of the packed sample and potential electrode electrolyte are high enough, $Z_x$ will become small (if $R_{ref}$ is also small) and result in negligible phase errors. However, a full analysis of phase errors with measured $C_{in}$ and $Z_x$ is necessary to judge if an uncorrected phase spectrum is acceptable or not across the range of HFs.

3.6.2 Variations of $C_{in}$ and implications for an approximate correction method

From all the column experiments, the $C_{in}$ obtained from each sample correction ranges from 8.3 to 9.7 pF and has a mean value 8.9±0.5 pF. The similarity of $C_{in}$ across all the measurements is consistent with our assumption that $C_{in}$ is only related to the
instrumentation and not impacted by the samples. As $C_{in}$ is a virtual capacitance concept that represents the PCC strength within the instrument, many environmental factors could cause $C_{in}$ variations, e.g., temperature, humidity and surrounding electronic devices, which explains the small variations of $C_{in}$ observed among different experiments.

The proposed phase correction method using multi-datasets of $-\phi_m$ collected under different $Z_x$ conditions is based on the condition that $C_{in}$ is not known in advance. If $C_{in}$ is already determined for an SIP instrument operating in a stable environment, the corrected phase can be simply obtained by subtracting $\omega C_{in}Z_x$ from $-\phi_m$ according to Eq. (3.15). This alternative correction method only needs one $-\phi_m / Z_x$ dataset, which results in less data acquisition time. However, as the predetermined $C_{in}$ and the true $C_{in}$ at the time of the correction will inevitably have some uncertain difference ($\Delta C_{in}$) due to the $C_{in}$ variations, the corrected phase using predetermined $C_{in}$ will contain an error $\omega \Delta C_{in}Z_x$. To evaluate the correction accuracy using only one $-\phi_m / Z_x$ dataset, we present the correction error uncertainty for two synthetic phase spectra considering $\Delta C_{in}$ has an uncertainty of $\pm 1$ pF (Figure 3.12). When using $-\phi_m$ collected at 20 kΩ $Z_x$, this correction error uncertainty is $\pm 2.5$ and $\pm 1.3$ mrad at 20 and 10 kHz, and then reduce to $\pm 0.13$ mrad at 1 kHz. We consider this error range small and acceptable, especially below 10 kHz. However, when using $-\phi_m$ collected at 100 kΩ $Z_x$, the correction error uncertainty will increase to be $\pm 12.6$, $\pm 6.3$ and $\pm 0.63$ mrad at 20, 10 and 1 kHz as it is proportional to $Z_x$. In this case, the correction error uncertainty is large and reduces the correction quality significantly.
Figure 3.12 Correction uncertainty due to the ±1 pF uncertainty of $C_{in}$ for two synthetic sample phase spectra. (a). Example of small phase response and (b). Example of large sample phase.

Figure 3.12 also shows that the significance of the same absolute correction error uncertainty will depend on its size relative to the true sample phase. For a sample with low phase response (e.g., Figure 3.12a), the correction error uncertainty using $-\phi_m / Z_x =100 \text{k}\Omega$ causes significant shape change of the phase spectrum above 1 kHz. When the sample has a high phase response (e.g., Figure 3.12b), the relative influence of correction uncertainty seems to be small and does not impact the spectrum shape significantly. The results show that, although the correction using predetermined $C_{in}$ and one $-\phi_m / Z_x$ dataset requires less time, there is a risk of a large correction error due to the small variations of $C_{in}$. This correction uncertainty is reduced as $Z_x$ decreases. However, $C_{in}$ is inherently uncertain and subject to change significantly. Therefore, we strongly recommend the proposed correction method using multiple $-\phi_m / Z_x$ datasets, which allows for precise determination of $C_{in}$ for each sample, thereby providing the highest quality SIP data possible.
3.6.3 Comparison with a two-electrode method

Impedance data above the four-electrode SIP (4-SIP) frequency range are usually acquired using a two-electrode impedance spectroscopy (2-IS) method, where voltages are measured via the same pair of electrodes as used for current injection (Volkmann & Klitzsch 2015). The 2-IS avoids the errors due to the PCC existing in 4-SIP and provides accurate impedance measurements above MHz frequencies. However, it results in large errors from electrode polarization when frequency decreases (Knight & Nur 1987). It has been observed in many studies that both 2-IS and 4-SIP cannot measure kHz range phase data accurately without appropriate corrections (e.g., Lesmes & Frye 2001; Volkmann & Klitzsch 2015; Loewer et al. 2017). The lack of reliable impedance data in the kHz frequency limits the understanding of electrical properties in the wideband frequency range.

To test if our 4-SIP correction method could produce consistent kHz range phase data relative to that from the 2-IS, the phase and dielectric constant spectra of 0.01 S/m NaCl fluid obtained from both types of measurements are combined from 1 Hz to 1 MHz (Figure 3.13). The 4-SIP data are the same as that used in Figure 3.8a. To acquire 2-IS data, the NaCl fluid was packed into a 5.6 cm diameter cylindrical sample holder with two parallel platinum plate electrodes installed at the top and bottom spaced 1.2 cm apart. The 2-IS data were collected from 1 kHz to 1 MHz using Agilent 4294A impedance analyzer. Figure 3.13a shows that 2-IS accurately measures the phase from 1 MHz until around 20 kHz, with large deviations from the theoretical curve below 20 kHz resulting from electrode polarization. As already discussed in Section 3.5.1, all the uncorrected 4-SIP phase spectra contain large errors at HFs and therefore cannot reach a continuous overlap with the 2-IS results. After correction, the 4-SIP phase successfully merges with the 2-IS data at
frequencies above 20 kHz. The combined phase spectrum using corrected 4-SIP (below 20 kHz) and 2-IS (above 20 kHz) agrees well with the theoretical phase curve except at LFs where the phase is very small (< 0.1 mrad) and cannot be reliably recorded by the SIP instrument.

Figure 3.13 Phase and dielectric constant spectra acquired from 4-SIP and 2-IS for the 0.01 S/m NaCl fluid. 4-SIP data are the same as that shown in Figure 3.8a. (Open circles: uncorrected 4-SIP; Red solid circles: corrected 4-SIP and Blue solid circles: 2-IS.)

Figure 3.13b shows the dielectric constant spectra calculated from the corresponding phase data in Figure 3.13a using Eq. (3.17). The dielectric constant obtained from 2-IS is around 80 (20 °C) at frequencies from 50 kHz to 1 MHz, and then gradually increases to 90 as frequency decreases towards 20 kHz. Below 20 kHz, the dielectric constant from 2-IS increases significantly due to the contribution from electrode polarization and becomes as high as 1700 at 1 kHz. Considering the 4-SIP measurement, uncorrected phase at kHz frequencies results in dielectric constant from 448 to 1256, which is 5.6 to 15.7 times than the expected value (i.e., 80). The corrected phase gives an accurate dielectric constant that agrees with 2-IS measurements. The abnormal increase of dielectric constant below 100 Hz is again attributed to the low sample phase which is below the instrument accuracy and
detection limit. Our results demonstrate that both uncorrected 4-SIP and 2-IS cannot measure the phase accurately from 100 Hz to 20 kHz. The proposed phase correction method for 4-SIP generates accurate phase data at kHz and results in a complete phase or dielectric spectrum over a wideband frequency range.

3.6.4 Implementation of phase correction method

To acquire accurate HF SIP data using the proposed correction method, several important issues are summarized below.

The proposed phase correction method only removes HF errors due to the interaction between the PCC and the sample holder, whereas other errors may exist when using a non-optimal instrument or sample holder. The instrument accuracy should be evaluated by a well-defined electric circuit or simply a high-quality resistor, from which it can be revealed if the instrument or the connection cables introduce any errors in the studied frequency range. Poorly designed sample holders may cause measurement errors by the electrode polarization from either current or potential electrodes (Zimmermann et al. 2008). Such errors can be evaluated by collecting SIP data on fluid samples at LFs. The instrument and sample holder used in this study do not show such errors according to the results in Figure 3.5 and Figure 3.8.

The proposed phase correction method is based on the simplified phase error model Eq. (3.15) that is only valid under certain conditions. To accurately use Eq. (3.15), the criteria justified in Section 3.2.3 should be considered and fulfilled. For example, the parameters
related to the phase correction were controlled during our experiments as described in Section 3.4.2. As the phase error model is derived based on an electric circuit representing a common SIP acquisition system, the correction method is expected to work well for other SIP instruments with similar configurations. Although we only tested the correction method on unconsolidated samples packed into a cylindrical sample holder, we believe it will work equally well for other types of SIP sample holders used for unconsolidated or consolidated samples. However, for simultaneous multi-channel SIP measurements via several pairs of potential electrodes (e.g., Zhang et al. 2012), the electric circuit model would need to be modified as more leakage current pathways are involved.

The simpler correction method using a predetermined $C_{in}$ and only one $-\phi_m / Z_x$ dataset can work well under certain conditions. One big advantage of this approach is the shorter acquisition time. Although we have shown that a small $C_{in}$ variation may cause significant correction uncertainty, this uncertainty is reduced when $-\phi_m$ data are collected at low $Z_x$ conditions (Figure 3.12). In addition, keeping the instrument operating in a stable environment (e.g., temperature, humidity) may reduce the $C_{in}$ variation, which subsequently reduces the correction uncertainty. However, it is important to include error bars to show the correction uncertainty when using a predetermined $C_{in}$. Frequent calibration of $C_{in}$ is also necessary to increase the reliability of corrected phase at HFs.

3.7 Conclusions

In this study, we applied an electrical circuit model to simulate the interaction between the SIP instrumentation PCC and sample holder and derived an equation showing that $-\phi_m$ in
SIP measurements is the sum of the true sample phase and a phase error term $\omega C_{in}Z_x$. For a packed unconsolidated sample, $-\phi_m$ spectra at HF conditions (by varying $L_{el}$ of potential electrode) are completely different, while LF $-\phi_m$ spectra are close to each other. This finding demonstrates that $-\phi_m$ at HF conditions contains errors and cannot be used for data interpretation without correction. Based on the linear relationship between $-\phi_m$ and $Z_x$ at each frequency, we developed a new phase correction method. The corrected HF phase of electrical circuits with modeled $Z_x$ and NaCl fluids result in errors less than 1 mrad even at 20 kHz. The correction method provides a more reliable phase spectrum at HF frequencies that can lead to improved understanding of the polarization mechanisms occurring in rocks and sediments in the kHz range, where it is traditionally very challenging to make reliable measurements using either 4-SIP or 2-IS techniques.

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Chapter 4  On Negative Induced Polarization in Frequency Domain Measurements

Abstract

Induced polarization (IP) has been widely used to non-invasively characterize electrical conduction and polarization in the subsurface resulting from an applied electric field. Earth materials exhibit a lossy capacitance defined by an intrinsic negative phase in frequency-domain IP (FDIP) or positive intrinsic chargeability in time-domain IP (TDIP). However, error-free positive apparent phase or negative apparent chargeability (i.e., negative IP effects) can occur in IP measurements over heterogeneous media. While negative IP effects in TDIP datasets have been discussed, no studies have addressed this topic in detail for FDIP measurements. We describe theory and numerical modeling to explain the origin of negative IP effects in FDIP measurements. A positive apparent phase may occur when a relatively high polarizability feature falls into negative sensitivity zones of complex resistivity measurements. The polarity of the apparent phase is determined by the distribution of subsurface intrinsic phase and resistivity, with the resistivity impacting the apparent phase polarity via its control on the sensitivity distribution. A physical explanation for the occurrence of positive apparent phase data is provided by an electric circuit model representing a four-electrode measurement. We also show that the apparent phase polarity will be frequency dependent when resistivity changes significantly with frequency (i.e. in the presence of significant IP effects). Consequently, negative IP effects manifest

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themselves in the shape of apparent phase spectra recorded with multi-frequency (spectral IP) datasets. Our results imply that positive apparent phase measurements should be anticipated and should be retained during inversion and interpretation of single frequency and spectral IP datasets.

4.1 Introduction

Induced polarization (IP), a non-invasive electrical geophysical technique for subsurface characterization, has been widely used in various fields including hydrogeology, engineering, mining exploration and environmental problems (e.g., Pelton et al. 1978; Slater & Lesmes 2002; Flores et al. 2012; Saneiyan et al. 2019). IP measures both electrical conduction (i.e., resistivity) and polarization in a porous medium, therefore providing additional information beyond the direct current resistivity method. The polarization is quantified by either a chargeability in time-domain IP (TDIP) or a phase in frequency-domain IP (FDIP) measurements (Binley & Kemna 2005). The intrinsic capacitive properties of Earth materials are characterized by a positive intrinsic chargeability (in TDIP) or a negative intrinsic phase when expressed in impedance or complex resistivity space (in FDIP). One would therefore expect a positive apparent (measured) chargeability, or equivalently a negative apparent (measured) phase, which we define here as the normal (or positive) recorded IP response (S. Ward 1988).

In field data acquisition, a negative IP response, i.e., a negative apparent chargeability or a positive apparent phase, is sometimes observed in the measurements. Such negative IP measurements are often treated as errors and deleted during the data inversion or
interpretation (e.g., Mary et al. 2016; Ntarlagiannis et al. 2016; Kelter et al. 2018; Garcia-Artigas et al. 2020). While negative IP responses may indeed reflect measurement artifacts, they can also result from the distortion of the electric field for certain types of heterogeneity close to the electrodes. Negative IP effects in TDIP measurements resulting from such effects have been investigated (Nabighian & Elliot 1976; Sumner 1976; Komarov 1980; Dahlin & Loke 2015). Dahlin & Loke (2015) conclude that negative apparent chargeability results when highly polarizable features fall within zones of negative resistivity measurement sensitivity for the utilized electrode configuration. They found that the resistivity distribution influences the occurrence and magnitude of negative apparent chargeability data. Such negative IP measurements provide information about the distribution of features in the subsurface and should not simply be removed during data processing (Binley 2015; Dahlin & Loke 2015).

Negative IP effects in FDIP have seldom been reported and studied. Luo and Zhang (1998) presented analytical solutions that predict a positive apparent phase for a buried polarizable sphere measured by a dipole-dipole array. Some recent complex resistivity imaging studies (Flores Orozco et al. 2018; Liu et al. 2017) reported positive apparent phase measurements and included them in the inversion per recommendations of Dahlin & Loke (2015) for TDIP datasets. Although frequency and time domain signals are in principle equivalent via the Fourier transform when the frequency/time range is adequately large, the two commonly measured IP parameters, FDIP apparent phase and TDIP apparent chargeability, are not directly equivalent.
The apparent chargeability equation developed by Seigel (1959), extended by V. Komarov and colleagues in Russia shortly after Seigel’s publication (Komarov 1960), provides a theoretical explanation for negative IP in TDIP measurements. To the knowledge of the authors, no equivalent formulation to explain the existence of negative IP in FD measurements has been presented. Considering the commonly established approximate proportionality between phase and chargeability (e.g., Van Voorhis et al. 1973; Lesmes & Frye 2001), we might expect similarities in the behavior of negative IP in FDIP measurements to that observed in TDIP reported by Dahlin & Loke (2015). However, the significance of negative IP effects in FDIP measurements remains poorly understood, especially with respect to spectral IP where the frequency dependence of IP measurements is recorded. In this study, we integrate theory, numerical modeling, equivalent electric circuits and laboratory measurements to comprehensively investigate negative IP effects in FDIP, including single frequency and spectral IP measurements.

4.2 Theory of negative IP effects

The intrinsic electrical properties of the subsurface are described by a complex resistivity ($\rho^*$) or its inverse, the complex conductivity ($\sigma^*$):

$$\rho^* = |\rho^*| e^{i\phi} = \frac{1}{\sigma^*},$$  \hspace{1cm} (4.1)

where $|\rho^*|$ is the complex resistivity magnitude, $\phi$ is the complex resistivity phase ($\phi \leq 0$) and $i$ is the imaginary unit with $i^2 = -1$. Both $\rho^*$ and $\sigma^*$ can also be presented in terms of real and imaginary components that are directly related to the physical (e.g., pore geometry) and chemical properties of the subsurface.
Field scale FDIP data are most commonly acquired using a four-electrode arrangement at the Earth surface. Two electrodes inject a known sinusoidal alternating electrical current ($\tilde{I}_0$) at various frequencies, while the other two electrodes record the resultant sinusoidal voltage (or potential difference, $\Delta \tilde{U}$). According to Ohm’s Law, the measured impedance $Z_{app}$ (with magnitude $|Z_{app}|$ and $\varphi_{app}$) is determined as,

$$Z^*_{app} = |Z^*_{app}|e^{i\varphi_{app}} = \frac{\Delta \tilde{U}}{I_0} = \frac{|\Delta \tilde{U}| \sin(\omega t + \varphi_{\Delta U})}{|I_0| \sin(\omega t)} = \frac{|\Delta \tilde{U}|}{|I_0|} e^{i\varphi_{\Delta U}},$$

(4.2)

where $\omega$ is the angular frequency, $t$ is time, $|I_0|$ is the current amplitude, $|\Delta \tilde{U}|$ is the voltage amplitude and $\varphi_{\Delta U}$ is the phase shift of the voltage sinusoid relative to the current sinusoid $\tilde{I}_0$ (defined as the zero phase reference). The apparent complex resistivity $\rho^*_{app}$ (with magnitude $|\rho^*_{app}|$ and the same phase $\varphi_{app}$ as that of $Z_{app}$) is determined using the geometric factor of the applied electrode array $K$,

$$\rho^*_{app} = |\rho^*_{app}|e^{i\varphi_{app}} = K Z^*_{app} = K |Z^*_{app}| e^{i\varphi_{app}}.$$  

(4.3)

$\rho^*_{app}$ is the complex resistivity of a homogeneous space equivalent to the value of $Z^*_{app}$ resulting from application of Eq. (4.3). Eqs. (4.2) and (4.3) show that $\rho^*_{app}$, $Z^*_{app}$, and $\Delta \tilde{U}$ are linearly related parameters with differing magnitude but the same phase value.

For a heterogeneous subsurface with a two-dimensional distribution of intrinsic complex resistivity $\rho^*$ (i.e., $\rho^*$ varies in horizontal $x$ and vertical $z$ but constant in $y$ direction), the potential $U$ at coordinate $(x, y, z)$ due to a point current source $I$ is described by the Fourier transformed Poisson’s equation (e.g., Kemna 2000; Binley 2015),
\[
\frac{\partial}{\partial x} \left( \frac{1}{\rho^*} \frac{\partial v^*}{\partial x} \right) + \frac{\partial}{\partial z} \left( \frac{1}{\rho^*} \frac{\partial v^*}{\partial z} \right) - \frac{v^* k^2}{\rho^*} = -I \delta(x) \delta(z), \quad (4.4)
\]

\[
U(x, y, z) = \frac{1}{\pi} \int_0^\infty v^*(x, k, z) \cos(ky) \, dk, \quad (4.5)
\]

where \( \delta \) is the Dirac delta function, \( v^* \) is the Fourier transformed complex voltage and \( k \) is the wave number. Eqs. (4.4) and (4.5) are solved numerically via discretization, for example using the finite element method. The superposition of calculated potentials at the potential (voltage recording) electrodes and application of Eqs. (4.2) and (4.3) yields the \( \rho_{\text{app}}^* \) of four-electrode measurements acquired over a heterogeneous \( \rho^* \) subsurface.

To investigate the occurrence of negative IP in FDIP (i.e., a positive \( \phi_{\text{app}} \)), we consider a subsurface modeled by a number of small cells with each cell \( j \) \( (j = 1, 2, \ldots, M) \) characterized by an intrinsic complex resistivity \( \rho_j^* \) (with magnitude \( |\rho_j^*| \) and phase \( \phi_j \)). If we consider cells parameterized in terms of the logarithms, \( \ln \rho_j^* \), and measurements equivalently expressed as \( \ln \rho_{\text{app}}^* \), then for a single four-electrode measurement, the sensitivity to the cell \( j \) \( (S_j^*) \) quantifies how the change in \( \ln \rho_j^* \) changes \( \ln \rho_{\text{app}}^* \),

\[
S_j^* = \frac{\partial \ln \rho_{\text{app}}^*}{\partial \ln \rho_j^*} = \frac{\partial \ln(|\rho_{\text{app}}^*| e^{\phi_{\text{app}} i})}{\partial \ln(|\rho_j^*| e^{\phi_j i})} = \frac{\partial (\ln|\rho_{\text{app}}^*| + \phi_{\text{app}} i)}{\partial (\ln|\rho_j^*| + \phi_j i)}, \quad (4.6)
\]

Different from a conventional direct current (DC) resistivity measurement, \( S_j^* \) of the FDIP measurement is a complex number. As the derivatives of the complex functions in Eq. (4.6) satisfy the Cauchy-Riemann conditions (Kemna 2000), the following sensitivity components can be expressed as the real part of \( S_j^* \):
\[ S_j = \frac{\partial \ln |\rho_{app}^*|}{\partial \ln |\rho_j^*|} = \frac{\partial \varphi_{app}}{\partial \varphi_j}. \] (4.7)

The imaginary part of \( S_j^* \) is,

\[ S_{j, \text{im}} = \frac{\partial \ln |\rho_{app}^*|}{\partial \varphi_j} = -\frac{\partial \varphi_{app}}{\partial \ln |\rho_j^*|}. \] (4.8)

Although we mainly focus on the discussion of a single four-electrode measurement, it should be noted that a matrix comprising of \( S_j \) from a sequence of four-electrode measurements is the Jacobian matrix used, for example, in a gradient-based inverse problem. In Eq. (4.7), the sensitivity expressed in terms of complex resistivity magnitude is equivalent to that obtained for DC resistivity measurements, which can take either positive or negative values. An increase of \( |\rho_j^*| \) in a positive \( S_j \) zone will increase \( |\rho_{app}^*| \), whereas an increase of \( |\rho_j^*| \) in a negative \( S_j \) zone will decrease \( |\rho_{app}^*| \). An equivalent pattern holds for the phase terms as shown in Eq. (4.7). To illustrate, assume that the subsurface space has zero phase (i.e., is non-polarizable), and thus \( \varphi_{app} = 0 \). If the phase of an arbitrary cell \( \varphi_j \) decreases slightly to a negative value (i.e., becomes polarizable), \( \varphi_{app} \) will decrease to be \( < 0 \) if this polarizable cell is located in a zone of positive \( S_j \). However, \( \varphi_{app} \) may increase to be \( > 0 \) (i.e., negative IP signal) if this polarizable cell is in a zone of negative \( S_j \). This provides a theoretical basis for the presence of positive \( \varphi_{app} \) (negative IP effects) in FDIP measurements, i.e., \( \varphi_{app} > 0 \) is possible although all \( \varphi_j \leq 0 \). The imaginary sensitivity (Eq. 4.8) plays a negligible role as shown later.
While the above arguments are based on the analysis of a single cell \( \varphi_j \) and \( S_j \), a more generalized way is to consider the collective impacts from all the cells. Kemna (2000) exploited the expression in Eq. (4.7) by forming a “final phase improvement” in the inversion of complex resistivity data once satisfactory matching of the resistivity magnitudes was achieved. Building on this, consider an expression for the inversion of phase angles using the Gauss-Newton approach (neglecting any damping or regularization for simplicity) (e.g., Kemna 2000; Binley 2015),

\[
[S^T S] \Delta m = S^T [d - F(m_k)] \tag{4.9}
\]

\[
m_{k+1} = m_k + \Delta m \tag{4.10}
\]

where \( S \) is the sensitivity matrix for a sequence of four-electrode measurements, \( d \) is a vector of measured data (\( \varphi_{\text{app}} \) in this case), \( F \) is the forward modeling operator, \( m \) is a vector of the model parameters (\( \varphi_j \) in this case), \( m_k \) and \( m_{k+1} \) are the model parameter set at iteration \( k \) and \( k+1 \), respectively, \( \Delta m \) is the model parameter update at iteration \( k \). Assuming that the inversion is achieved with only one step from a starting model with all \( \varphi_j = 0 \), we have \( m_k = 0, F(m_k) = 0, m_{k+1} = \Delta m \). We can then write Eq. (4.9) as,

\[
S \Delta m = d. \tag{4.11}
\]

In this simplified one-step inversion, \( \Delta m \) is essentially the final model that matches \( d \). Again, if we only consider a single four-electrode measurement, Eq. (4.11) gives,

\[
\sum_{j=1}^{M} S_j \varphi_j = \varphi_{\text{app}}. \tag{4.12}
\]

This approximation describes the collective impacts of \( \varphi_j \) and \( S_j \) from all the cells. Eq. (4.12) explicitly shows that even when all \( \varphi_j \leq 0 \) \( (j = 1, 2, \ldots, M) \), \( \varphi_{\text{app}} \) can be positive when
relatively more negative $\varphi_j$ cells concurrently have $S_j < 0$. The polarity of $\varphi_{\text{app}}$ will therefore depend on the relative values of intrinsic phase and the sensitivity, where the latter is affected by the quadrupole geometry and distribution of the intrinsic resistivity.

A similar association between negative IP signals and the sensitivity distribution is recognized in TDIP data (T. Dahlin & Loke 2015). In TDIP, a unidirectional current is driven between the current electrodes for a period of time and then abruptly switched off. The voltage $V_p$ recorded right before switching off is used to obtain the apparent DC resistivity $\rho_{\text{app}}^{(\text{DC})}$ (assuming the current injection is long enough to approximate a DC condition). After switching off the current, $V_p$ drops suddenly to a secondary voltage $V_s$, which then decays with time. Seigel (1959) defined the apparent chargeability ($m_{\text{app}}$) as the ratio of $V_s$ to $V_p$ to quantify the TDIP polarization strength. Considering the same scenario where the subsurface is modeled by $M$ small cells with index $j$, the theoretical relationship between a single measure of $\rho_{\text{app}}^{(\text{DC})}$ and $m_{\text{app}}$, and the intrinsic parameters $\rho_j^{(\text{DC})}$ and $m_j$ making up the subsurface is (Seigel, 1959),

$$m_{\text{app}} = \sum_{j=1}^{M} \frac{\partial \ln \rho_{\text{app}}^{(\text{DC})}}{\partial \ln \rho_j^{(\text{DC})}} m_j = \sum_{j=1}^{M} S_j^{(\text{DC})} m_j. \quad (4.13)$$

where $S_j^{(\text{DC})}$ is the sensitivity to a cell $j$ in terms of DC resistivity, being analogous to the sensitivity in terms of complex resistivity magnitude (Eq. 4.7). Eq. (4.13) has essentially the same structure as Eq. (4.12). With all $m_j \geq 0$ ($j = 1, 2, \ldots, M$) for Earth materials, the polarity of $m_{\text{app}}$ is decided by the polarity of $S_j^{(\text{DC})}$ and the relative values of $m_j$. Eq. (4.13) predicts that negative $m_{\text{app}}$ is possible when features with relatively high $m_j$ fall into
negative sensitivity zones, providing theoretical support for the negative IP effects in TDIP. In practice, $m_{\text{app}}$ defined by Seigel (1959) is difficult to measure and an integral chargeability is instead commonly measured (Binley 2015), which can exhibit equivalent negative IP effects (T. Dahlin & Loke 2015).

We stress that laboratory measurements of intrinsic complex resistivity or chargeability on a core or soil sample (considered homogeneous at the measurement scale but in fact likely to contain small scale heterogeneity) can never exhibit negative IP effects when 1D current flow is maintained. Such negative IP effects sometimes reported in the literature (e.g., Abdulsamad et al. 2016; Saneiyan et al. 2018; Bate et al. 2020) can only arise from measurement errors.

4.3 Numerical modeling

To investigate the behavior of the $\phi_{\text{app}}$ polarity, 2D forward modeling of synthetic intrinsic complex resistivity distributions was performed using cR2 (http://www.es.lancs.ac.uk/people/amb/Freeware/cR2/cR2.htm) in its python wrapper ResIPy (Blanchy et al. 2020). The region of interest of the synthetic model contains 25 electrodes spaced 2 m apart for a total length of 48 m and extends to 8 m depth (Figure 4.1). A quadrilateral mesh with each mesh cell of size $0.25 \times 0.25$ m (i.e., 8 nodes per electrode) was used for the computations. In this case, each mesh cell corresponds to a small cell $j$ described in Section 4.2. This mesh extends a large distance beyond the region of interest and incorporates boundary conditions that approximate an infinitely large model space. Different intrinsic resistivity and phase values were assigned to different regions to
illustrate specific aspects of negative IP effects predicted by theory. Forward models were run to determine $\varphi_{app}$ of either a single four-electrode measurement or to construct a pseudosection from a sequence of measurements. The four electrodes include a pair of electrodes (positive C+ and negative C-) for current injection and a pair of electrodes (positive P+ and negative P-) for voltage (potential) measurements.

Figure 4.1 Numerical modeling set up with 25 electrodes (E1 to E25) on a model space using $0.25 \times 0.25$ m mesh cells.

The sensitivity distribution for a single four-electrode measurement on a selected synthetic model was computed using cR2, with a vector of $S_j^*$ corresponding to each mesh cell in the modeling space as the output (Eq. 4.6). No noise was added to the forward modeling and sensitivity distribution calculation so as to avoid the complicating effects of random errors on the modeling results.

4.3.1 Influence of sensitivity distribution

The sensitivity distribution for a dipole-dipole array (E10=C+, E12=C-, E14=P-, E16=P+) and also for a Wenner array (E10=C+, E12=P+, E14=P-, E16=C-) was first computed for a homogeneous, low polarizability half-space ($|\rho^*| = 100 \, \Omega \, m$, $\varphi = -1$ mrad) (Figure 4.2).

The imaginary sensitivity (Eq. 4.8, Figure 4.2c and 4.2d) exerts a negligible control on the
measurements as its values are many orders of magnitude less than the real sensitivity (Eq. 4.7, Figure 4.2a and 4.2b). A simulation on a homogenous, high polarizability half-space ($|\rho^*|=100 \, \Omega \, m$, $\varphi = -100 \, \text{mrad}$) results in similar negligible response in the imaginary sensitivity distribution, again being many orders of magnitude less than the real sensitivity.

We therefore refer to the real sensitivity in all future discussion of sensitivity patterns. Different patterns of positive and negative sensitivity are observed for the dipole-dipole (Figure 4.2a) and Wenner arrays (Figure 4.2b). The sensitivity of zones away from the electrode array is close to zero, therefore having a negligible effect on the $\rho_{\text{app}}$ measurement.

![Figure 4.2](image)

Figure 4.2 Sensitivity distribution of complex resistivity measurements using electrodes E10, E12, E14 and E16 for a 100 $\Omega \, m$ and $-1 \, \text{mrad}$ homogeneous half space. (a) Real sensitivity of dipole-dipole array (E10=C+, E12=C-, E14=P-, E16=P+). (b) Real sensitivity of Wenner array (E10=C+, E12=P+, E14=P-, E16=C-). (c) Imaginary sensitivity of dipole-dipole array. (d) Imaginary sensitivity of Wenner array.

To illustrate the influence of the sensitivity distribution on the polarity of the measured phase, new forward models were run where $\varphi_{\text{app}}$ of a single measurement using E10, E12, E14 and E16 was computed with a small polarizable cell ($|\rho^*|=100 \, \Omega \, m$ and $\varphi = -100 \, \text{mrad}$) of the same size as a mesh cell (0.25 $\times$ 0.25 m) placed at various locations in a background
non-polarizing half space ($|\rho^*| = 100 \, \Omega \, m, \varphi = 0 \, \text{mrad}$) (Figure 4.3a). Starting from the first mesh cell, the polarizable cell was moved to the right and down one cell by one cell to cover the horizontal distance from 15 to 24 m and the depth range from 0 to 6 m (containing the zone of enhanced sensitivity). With the polarizable cell at each mesh cell location, the apparent phase $\varphi_{\text{app}}$ of a dipole-dipole array (E10=C+, E12=C-, E14=P-, E16=P+) and a Wenner array (E10=C+, E12=P+, E14=P-, E16=C-) was computed. Figure 4.3 shows $\varphi_{\text{app}}$ plotted against the sensitivity of the location with the polarizable cell for the corresponding measurement array. The polarity of $\varphi_{\text{app}}$ is the inverse of the polarity of the sensitivity, i.e., the polarizable cell placed in positive sensitivity zones results in negative $\varphi_{\text{app}}$ and the polarizable cell placed in negative sensitivity zones results in positive $\varphi_{\text{app}}$. The magnitude of the negative IP signal increases linearly with the magnitude of the negative sensitivity.
4.3.2 Influence of heterogeneity

We next investigate the effect of heterogeneity on the sensitivity and hence the $\phi_{app}$ polarity pattern. A $3 \times 3$ m polarizable block was located between 22.5 m and 25.5 m along the line and placed at a depth of 0 m to 3 m (Figure 4.4a). The background was set with
φ_{bgk} = -1 \text{ mrad (low polarization)} \text{ and } |\rho_{bgk}^*| = 100 \ \Omega \text{ m, while the polarizable block was assigned } \varphi_{block} = -100 \text{ mrad and } |\rho_{block}^*| \text{ equal to either 50, 100 or 200 } \Omega \text{ m. For each } |\rho_{block}^*| \text{ scenario, a } \varphi_{app} \text{ pseudosection was computed for a dipole-dipole array sequence with } a = 4 \text{ m and } n = 1, 2, 3 \text{ and } 4 \text{ (i.e., electrodes placed in the order C+, C-, P-, P+ with spacing } a, a \times n \text{ and } a \text{ between C+ and C-, C- and P-, and P- and P+, respectively) (Figure 4.4b). The results show that the resistivity of the polarizable block has a significant influence on the polarity and magnitude of } \varphi_{app} \text{ within the zones indicated by the dashed triangles. These } \varphi_{app} \text{ values increase from negative to positive (i.e. negative IP effect) as } |\rho_{block}^*| \text{ increases from 50 to 100 } \Omega \text{ m. Higher positive values of } \varphi_{app} \text{ (i.e., enhanced negative IP effects) are observed for } |\rho_{block}^*| \text{ equal to 200 } \Omega \text{ m.}
Figure 4.4 Influence of resistivity heterogeneity on the $\phi_{app}$ polarity. (a). Synthetic model settings. (b). Pseudo section of $\phi_{app}$ at various values of $|\rho^*_\text{block}|$ ($|\rho^*_\text{block}| = 100 \ \Omega \ m$ is the homogeneous resistivity condition); data within the dashed triangles are influenced by $|\rho^*_\text{block}|$. (c). Sensitivity distribution of the single four-electrode measurement pointed out by the arrow in (b) with various $|\rho^*_\text{block}|$ corresponding to the pseudosections. (d). Sensitivity difference relative to that of $|\rho^*_\text{block}| = 100 \ \Omega \ m$.

This control of the resistivity of the heterogeneity on the polarity of $\phi_{app}$ results from how the presence of the heterogeneity modifies the sensitivity distribution relative to a homogeneous resistivity medium. To illustrate this, a single $\phi_{app}$ measurement using E10=C+, E12=C-, E14=P-, E16=P+ (pointed out by arrows in Figure 4.4b) is used as an
example. The corresponding sensitivity distribution for the three synthetic models with different $|\rho^{*}_{\text{block}}|$ values is shown in Figure 4.4c. As $|\rho^{*}_{\text{block}}|$ increases from 50 to 100, and then to 200 $\Omega$ m, $\varphi_{\text{app}}$ increases from $-14$ mrad to 9 mrad for the 100 $\Omega$ m block and to 33 mrad for the 200 $\Omega$ m block. This increase of $\varphi_{\text{app}}$ toward more positive values with increasing $|\rho^{*}_{\text{block}}|$ can be explained by the expansion of the negative sensitivity zones within the polarizable block boundary as $|\rho^{*}_{\text{block}}|$ increases (Figure 4.4c). This change in the sensitivity pattern is highlighted by the difference in sensitivity referenced to the sensitivity for the $|\rho^{*}_{\text{block}}|=100$ $\Omega$ m scenario, where $|\rho^{*}_{\text{block}}|=50$ $\Omega$ m and $|\rho^{*}_{\text{block}}|=200$ $\Omega$ m highlights increased and decrease sensitivity respectively within the block boundary (Figure 4.4d). This confirms that the resistivity heterogeneity has a significant influence on the polarity of $\varphi_{\text{app}}$ by changing the sensitivity distribution.

So far, we have shown that the polarity of $\varphi_{\text{app}}$ is determined by three major factors: (1) the location of polarizable objects relative to positive/negative sensitivity zones; (2) the intrinsic phase of the polarizable objects relative to the surrounding subsurface; (3) the subsurface resistivity heterogeneity that changes the sensitivity patterns. To illustrate the collective impacts of the intrinsic resistivity and intrinsic phase, we computed $\varphi_{\text{app}}$ for a dipole-dipole array (E10=C+, E12=C-, E14=P-, E16=P+) using the same model structure and background settings as shown in Figure 4.4a, but with $|\rho^{*}_{\text{block}}|$ varying from 20 to 200 $\Omega$ m and $\varphi_{\text{block}}$ varying from $-5$ to $-120$ mrad (Figure 4.5a). When $|\rho^{*}_{\text{block}}|=20$, 40 or 60 $\Omega$ m, all $\varphi_{\text{app}}$ are negative and become more negative with $\varphi_{\text{block}}$ changing from $-5$ to $-120$ mrad. When $|\rho^{*}_{\text{block}}|=80$, 100, 120 or 140 $\Omega$ m, $\varphi_{\text{app}}$ is negative when $\varphi_{\text{block}}$ is small ($-5$ mrad), but becomes positive when $\varphi_{\text{block}}$ is more negative. At $|\rho^{*}_{\text{block}}|$ above 140 $\Omega$ m, all
φ_app are positive even when φ_block is only −5 mrad; again, φ_app becomes more positive as φ_block becomes more negative. A clear transition from negative φ_app to positive φ_app can be observed in Figure 4.5a, which shows that a higher |ρ^block| relative to |ρ^bgk| tends to result in positive φ_app. The φ_app pattern will also be affected by other factors, for example the background phase φ_bgk. Figure 4.5b presents the φ_app change when φ_bgk is set to be −10 mrad. In this situation, more points show negative φ_app with positive φ_app only occurring when |ρ^block| is sufficiently large and φ_block is sufficiently negative.

Figure 4.5 Impacts of |ρ^block| and φ_block on the modeled φ_app under various conditions. (a) and (b). φ_app modeled using a dipole-dipole array (E10=C+, E12=C-, E14=P-, E16=P+) for the synthetic structure shown in Figure 4.4a under various background settings (indicated by dotted and dashed lines). (c). φ_app modeled with the same settings as (a) but with vertical extent of polarizable block in Figure 4.4a reduced to be between 0 and 1 m.

The shape of the polarizable block also determines the φ_app change under various |ρ^block| and φ_block conditions. Figure 4.5c shows the simulation with the same model settings as that in Figure 4.5a except that the vertical extent of the polarizable block is reduced to be between 0 to 1 m. In this case, most of the points show positive φ_app due to the increased portions of negative sensitivity zone in the polarizable block. For example, in the case of |ρ^block| = 100 Ω m in Figure 4.4c, when the vertical extent of the polarizable block is
reduced to be between 0 to 1 m, most of the regions within the block would have negative sensitivity. In this situation, positive $\varphi_{app}$ is more likely as per Eq. (4.12).

The above results were obtained from simple, heterogenous synthetic models. For a real subsurface, the interactions between complicated structures and zones may result in various $\varphi_{app}$ patterns, making it difficult to generalize about what situations will result in negative IP effects. One important observation from Figure 4.5 is that even weakly polarizable objects (e.g., $\varphi_{\text{block}} = -5$ and $-10$ mrad) may produce negative IP signals, especially when the objects have high resistivity relative to the background (e.g., polarizable objects characterized by low water content, low porosity or high electrical resistivity pore fluids).

4.4 A physical explanation of negative IP effects using an electrical circuit

We have so far explained the occurrence of negative IP signals using theory and numerical modeling. Next, we seek a more physical explanation as a positive phase implies that the electrical current lags the voltage, which is considered to be non-physical in the presence of IP effect. We use a simplified electrical circuit model to provide a physical explanation for negative IP effects. We consider a subsurface represented by a resistor/impedance network circuit (Figure 4.6a). A sinusoidal current $\vec{I}_0$ with fixed amplitude $|\vec{I}_0|$ and zero reference phase is injected between C+ and C-, while the resultant sinusoidal voltage $\Delta \vec{U}$ (with amplitude $|\Delta \vec{U}|$ and phase $\varphi_{\Delta U}$) is measured between P+ and P- in the same manner as a dipole-dipole array. Comparing the relative locations of the circuit components in Figure 4.6a with Figure 4.2a, $Z\tilde{I}$ (with magnitude $|Z\tilde{I}|$ and phase $\varphi_1$) and $Z\tilde{Z}$ (with magnitude $|Z\tilde{Z}|$ and phase $\varphi_2$) represent impedance components located in the positive and negative
sensitivity zones, respectively. We next evaluate how changes of $Z_1^*$ or $Z_2^*$ alter the apparent measured impedance $Z_{app}^*$ (i.e., $\delta \bar{U}/\bar{I}_0$).

Figure 4.6 Electrical circuit model to explain the negative IP effects. (a). Electrical conduction through the subsurface modeled as a resistor/impedance network circuit; grey arrows illustrate idealized current flow directions in a real subsurface space for comparison; (b) A simplified equivalent linear electrical circuit of the circuit conceptualized in (a).

To make the analysis simple, we set all other circuit components to be pure resistors (represented by symbol ‘R’). According to Figure 4.6a, $\bar{I}_0$ exits the network via ‘C-’ by passing $Z_1$, $Z_2$, $R_3$, $R_4$ and $R_5$, which gives $\bar{I}_0 = \bar{I}_1 + \bar{I}_4 + \bar{I}_2$ with $\bar{I}_2 = \bar{I}_3 + \bar{I}_5$, where $\bar{I}_1$ to $\bar{I}_5$ are the currents flowing through the corresponding impedance/resistors. We simplify this network circuit to an equivalent linear circuit that is easier to analyze (Figure 4.6b). In Figure 4.6b, $R_{3s}$, $R_{4s}$ and $R_{5s}$ represent the equivalent total resistances of the current path prior to $R_3$, $R_4$, and $R_5$ respectively, while other components are identical to those shown in Figure 4.6a. The total impedance of this circuit is,
where $\bar{U}_0$ is the total voltage between C+ and C- and $a$ and $b$ are real number constants as resistances $R_{3s}, R_{3s}, R_{4s}, R_{4}, R_{5s}$ and $R_{5}$ do not change. According to the voltage divider rule,

$$\frac{\Delta \bar{U}}{\bar{U}_0} = \frac{R_3}{(R_{3s} + R_3)} b + Z_2^* = c \frac{b}{b + Z_2^*},$$

where $c$ is again a real number constant representing a constant resistance term. Combining Eq. (4.2), Eq. (4.14) and (4.15) gives,

$$|Z_{app}^*| e^{\varphi_{app}} = \frac{\Delta \bar{U}}{T_0} = \frac{bc}{b + Z_2^* + aZ_2^* + ab + 1}. \tag{4.16}$$

Considering that the intrinsic phase shifts of the earth materials are small negative values ($-0.2 < \varphi < 0$), $\cos \varphi \approx 1$ and $\varphi \approx \sin(\varphi) \approx \tan(\varphi) \approx \tan^{-1}(\varphi)$. Any impedance term $Z^*$ can then be written in rectangular form as $Z^* \approx |Z|\cos(\varphi) + i|Z|\sin(\varphi) \approx |Z| + i|Z|\varphi$. When $Z_1^*$ (located in the positive sensitivity zone of the array) is polarizable (i.e., $\varphi_1 < 0$) and $Z_2^*$ (located in the negative sensitivity zone) is non-polarizable (i.e., $\varphi_2 = 0$), Eq. (4.16) gives,

$$\varphi_{app} \approx \varphi_1 \frac{b + |Z_2^*|}{b + |Z_2^*| + a|Z_1^*||Z_2^*| + ab|Z_1^*| + |Z_1^*|}, \tag{4.17}$$

which explicitly shows that $\varphi_{app} < 0$, being a measurement signal with normal polarity. On the contrary, if $Z_2^*$ is polarizable (i.e., $\varphi_2 < 0$) and $Z_1^*$ is non-polarizable (i.e., $\varphi_1 = 0$), Eq. (4.16) results in,
\[
\varphi_{\text{app}} \approx -\varphi_2 \frac{|Z_2^*| + a|Z_1^*||Z_2^*|}{b + |Z_2^*| + a|Z_1^*||Z_2^*| + ab|Z_1^*| + |Z_1^*|},
\]

which gives \(\varphi_{\text{app}} > 0\), being a measurement signal with negative IP polarity. It can be concluded that the negative IP signals originate from the fact that the impedance is determined from dividing the recorded voltage \(\Delta \hat{U}\) by the input current \(\hat{I}_0\) instead of by the current flowing through the impedance across which \(\Delta \hat{U}\) is recorded, i.e., \(\hat{I}_3\) in our case. It is the phase difference between \(\hat{I}_3\) and measured \(\hat{I}_0\) that gives the non-physical impression of the current lagging the voltage as implied by a positive phase. The circuit model analogy also explains the impact of sensitivity on the resistivity measurements (i.e., resistance measurement in the circuit model). Considering \(Z_1^*\) and \(Z_2^*\) as pure resistors (i.e., zero phase), Eq. (4.16) shows that \(|Z_{\text{app}}^*|\) increases with the increase of \(|Z_1^*|\), whereas it decreases with the increase of \(|Z_2^*|\).

4.5 Frequency dependence

The influence of resistivity and phase variability on the polarity of \(\varphi_{\text{app}}\) also has important, hitherto unrecognized, implications for the interpretation of spectral IP datasets. The \(\varphi_{\text{app}}\) polarity can vary with frequency if the resistivity of polarizable features changes significantly with frequency, e.g., as observed for electronically conducting materials (e.g., Pelton et al. 1978; Wong 1979). We examine this effect using the same synthetic model structure shown in Figure 4.4a but assigning various values of frequency independent \(|\rho_{\text{bgk}}^*|\), \(\varphi_{\text{bgk}}\) and frequency-dependent \(|\rho_{\text{block}}^*|\) and \(\varphi_{\text{block}}\). We define the frequency dependence of the polarizability of the block using a Cole-Cole type model (Cole & Cole 1941; Pelton et al. 1978) with parameters previously found to fit laboratory experimental data obtained on
a zero valent iron-sand mixture (50% iron by volume) (Slater et al. 2005) (Figure 4.7a). The spectra cover frequencies from $10^{-3}$ to $10^4$ Hz, with $|\rho_{\text{block}}|$ decreasing from 41 to 14 $\Omega$ m (from low to high frequency). The $\varphi_{\text{block}}$ ranges from $-21$ mrad to $-174$ mrad, with the peak occurring at $-1$ Hz. The frequency independent background half-space was assigned $\varphi_{\text{bgk}} = -1$ mrad, with the $|\rho_{\text{bgk}}|$ set to either 10, 30 or 55 $\Omega$ m in order to simulate scenarios with $|\rho_{\text{bgk}}|$ lower, close to or higher than $|\rho_{\text{block}}|$ (Figure 4.7a).

![Figure 4.7](image)

Figure 4.7 Simulation based on a polarizable block with frequency-dependent complex resistivity using model structure shown in Figure 4.4a. (a). Intrinsic resistivity and phase spectra of the polarizable block and the selection of frequency-independent background resistivity (colored dashed lines); black dashed line represents $\varphi_{\text{block}} = 0$ mrad; (b). $|\rho_{\text{app}}|$ and $\varphi_{\text{app}}$ spectra under different $|\rho_{\text{bgk}}|$ conditions; black dashed line represents $\varphi_{\text{app}} = 0$ mrad.

Figure 4.7b shows the apparent parameters $|\rho_{\text{app}}|$ and $\varphi_{\text{app}}$ from the single measurement for a dipole-dipole array (E10=C+, E12=C-, E14=P-, E16=P+) at various frequencies. Three simulations result in completely different shapes of $\varphi_{\text{app}}$ curves when only the resistivity contrast between the target and the background changes between the simulations. For the
highest background resistivity, $|\rho_{bgk}| = 55 \, \Omega \, m$, the $\varphi_{app}$ spectra are negative and display a negative peak similar to the $\varphi_{block}$ spectrum. When $|\rho_{bgk}^*|$ is reduced to 30 $\Omega$ m, $\varphi_{app}$ is negative at high frequencies but increases to be positive below around 20 Hz. Peaks are observed in both positive and negative apparent phase domains. For the lowest background resistivity $|\rho_{bgk}^*| = 10 \, \Omega$ m, all $\varphi_{app}$ values become positive and a peak of $\varphi_{app}$ toward more positive values is observed.

The differences among the three $\varphi_{app}$ curves can be explained by the difference in resistivity of $|\rho_{block}^*|$ relative to $|\rho_{bgk}^*|$ and how this difference affects the sensitivity distribution, as demonstrated in Section 4.3.2. Positive $\varphi_{app}$ values are found when $|\rho_{block}^*|/|\rho_{bgk}^*|$ is relatively high, being the case when $|\rho_{bgk}^*| = 10 \, \Omega$ m for all frequencies and when $|\rho_{bgk}^*| = 30 \, \Omega$ m at low frequencies. The $|\rho_{app}^*|$ spectra also differ between the three simulations, exhibiting a frequency dependence consistent with the polarity of $\varphi_{app}$. The percentage frequency effect (PFE = ($|\rho_{app}^*|_L - |\rho_{app}^*|_H$) / $|\rho_{app}^*|_L$, where subscripts $H$ and $L$ refer to a high and low measurement frequency, respectively) is another measure of the IP effect that was popular in mineral exploration (S. Ward 1988). Figure 4.7b shows that a negative PFE (i.e., increasing $|\rho_{app}^*|$ with increasing frequencies) is always observed when $\varphi_{app}$ is positive. Just as with positive $\varphi_{app}$ values, a negative PFE is non-physical from the perspective of IP mechanisms and another representation of negative IP effects in frequency domain IP measurements.

In summary, this simulation of frequency dependent data demonstrates the possibility of a wide range of $\varphi_{app}$ spectra, which can be very different from the spectra of an intrinsic
polarizable target. This has significant implications with respect to the interpretation of field-measured phase curves.

4.6 Sandbox experiments

Laboratory sandbox experiments were conducted to verify the observations from numerical modeling (Figure 4.8a). A sandbox 36 cm wide, 15 cm high and 55 cm long was filled with sand fully saturated with tap water (resistivity of 40 Ω m at 25 °C). Four electrodes were deployed in the central area of the sandbox with a 5 cm spacing. The distance between the electrodes and the box wall was large enough to ignore boundary effects on the measurements. FDIP (from 0.1 to 100 Hz) and TDIP data (1 Hz waveform) were measured using an Ontash & Ermac PSIP instrument and an IRIS Syscal Pro instrument, respectively. $\varphi_{\text{app}}$ and $M_{\text{app}}$ of the background sand was –2 mrad and 2 mV/V respectively, providing a low polarizability background matrix.
Figure 4.8 Sandbox experiments. (a) Schematic diagram of sandbox experimental set-up. (b). $|\rho_{app}^{*}|$ and $\varphi_{app}$ spectra measured by dipole-dipole! array; black dashed line represents $\varphi_{app} = 0$ mrad (c) $|\rho_{app}^{*}|$ and $\varphi_{app}$ spectra measured by Wenner array; black dashed line represents $\varphi_{app} = 0$ mrad.

To simulate a scenario similar to the synthetic model in Section 4.5, a piece of the iron mineral magnetite (dimensions approximately 8 cm length, 4 cm height and 5 cm width) was buried between the middle two electrodes at 2 cm depth. The $\varphi_{app}$ collected using the dipole-dipole array is negative at high frequencies and then increases to positive values below 4 Hz (Figure 4.8b). The spectral shape of $\varphi_{app}$ in Figure 4.8b is similar to the shape of the 0.1-200 Hz segment of the simulated blue $\varphi_{app}$ curve ($|\rho_{bgk}| = 30 \Omega$ m) in Figure 4.7b. The $M_{app}$ measured with the dipole-dipole array is $-42.5$ mV/V, also indicating a negative
IP response. Its polarity is consistent with the $\varphi_{\text{app}}$ polarity at low frequencies. For the Wenner array measurement, a conventional negative $\varphi_{\text{app}}$ spectrum is observed (Figure 4.8c) as the polarizable magnetite falls within the positive sensitivity zones of this array (Figure 4.2b). The $M_{\text{app}}$ measured by the Wenner array is positive (27.8 mV/V), being consistent with the negative $\varphi_{\text{app}}$ recorded in the frequency domain. These laboratory experiments therefore confirm the observations from numerical modeling and theory.

4.7 Conclusions

In a heterogenous polarizable subsurface the apparent phase $\varphi_{\text{app}}$ recorded in surface four-electrode FDIP measurements may be positive. The polarity of $\varphi_{\text{app}}$ is associated with the sensitivity distribution of a four-electrode measurement layout and is determined by the intrinsic phase and resistivity of the subsurface. Considerations of the sensitivity patterns of complex resistivity measurements theoretically confirm the occurrence of positive $\varphi_{\text{app}}$, i.e., for a non-polarizable subsurface, placing a small, highly polarizable object in the negative and positive sensitivity zones will result in positive and negative $\varphi_{\text{app}}$, respectively. This is consistent with a simplified electric circuit model, which physically explains the negative IP (i.e., the paradox of current appearing to lag voltage) to result from the measured voltage drop across the potential electrodes being divided by the input current at the current electrodes instead of the current flowing through the impedance across the potential electrodes.

Numerical modeling shows the $\varphi_{\text{app}}$ polarity is dictated by the relative values of both the intrinsic phase and the intrinsic resistivity of a polarizable heterogeneity compared to the
background medium. The control of the relative strength of the intrinsic resistivity on $\varphi_{\text{app}}$ results from its influence on the sensitivity distribution of a measurement. In the case that the intrinsic resistivity varies significantly with frequency, the $\varphi_{\text{app}}$ polarity can vary with frequency in FDIP measurements, which results in $\varphi_{\text{app}}$ spectra that are very different from the intrinsic phase spectrum. This finding is confirmed by laboratory sandbox experiments where $\varphi_{\text{app}}$ of a dipole-dipole array on a buried piece of magnetite is negative from 100 to 4 Hz and then becomes positive below 4 Hz. Our results emphasize the need to accurately quantify error sources in FDIP measurements as positive $\varphi_{\text{app}}$ measurements should be expected, are likely to be common in heterogeneous systems and should not simply be discarded prior to further data processing e.g. inversion. This observation is consistent with previously studied negative apparent chargeability data in TDIP measurements.

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Chapter 5  Characterizing Physical Properties of Streambed Interface Sediments using In Situ Complex Electrical Conductivity Measurements\(^1\)

Abstract
Streambed sediment physical properties such as surface area, are difficult to quantify in situ but exert a high-level control on a wide range of biogeochemical processes and sorption of contaminants. We introduce the use of complex electrical conductivity (CC) methods (also known as spectral induced polarization (SIP)) that measure both real and imaginary conductivity to non-invasively and efficiently characterize shallow streambed sediments. We explore the method through synthetic modeling, laboratory, and field measurements to demonstrate the sensitivity of imaginary conductivity to sediment surface area, controlled in part by fine-grained iron oxides produced by anoxic groundwater discharge. Laboratory measurements verify expected relationships between CC parameters and sediment properties. Synthetic modeling using a 1D analytical model illustrates the influence of water layer depth and conductivity on the field CC measurements made at the streambed-stream water interface. Specifically, the inverted sediment imaginary conductivity is less impacted by uncertainty in the water layer depth and conductivity relative to the real conductivity and phase shift. Field CC measurements along a landfill-impacted river reveal discrete streambed zones with enhanced bulk surface area generally

corresponding to anoxic groundwater discharges zones with high concentrations of fine-grained iron oxide precipitates.

5.1 Introduction
The physical properties of streambed sediments influence stream chemistry and ecology by regulating groundwater-surface water exchange processes and coupled biotic/abiotic redox reactions (Gandy et al. 2007, Sawyer & Cardenas 2009, Nogaro et al. 2010). Sediment surface area, grain size distribution, and cation exchange capacity (CEC) are closely related physical properties that determine average contact time between streambed pore fluids and bio-reactive surfaces (Findlay & Sobczak, 2000), influence streambed microbial communities (Mendoza-Lera et al. 2017), and control the quantity of streambed sorption sites (Bencala 1983). They also influence stream concentration-discharge relationships (Hoagland et al. 2017), nitrate concentration variations (Krause et al. 2009) and water/gas fluxes through the streambed (Vidon et al. 2010). Existing methodologies to characterize such streambed physical properties typically rely on destructive core-based sampling, providing limited spatial coverage and poor temporal information.

Electrical geophysical methods that non-invasively measure the bulk sediment electrical conductivity (i.e., inverse of resistivity) are sensitive to the physical properties of porous media and therefore have the potential for rapid in situ characterization of these elusive streambed material properties (Briggs et al., 2018). Direct current (DC) electrical resistivity and electromagnetic methods have been applied to investigate stream and river beds, although the focus has been on detecting and monitoring groundwater-surface water
exchange (e.g., review by McLachlan et al., 2017). By exploiting the electrical conductivity contrast between groundwater, surface water and/or a tracer, the method has been used in the bed of streams, rivers and lakes to identify localized groundwater discharges (Nyquist et al. 2008), delineate the extent of the hyporheic zone (Ward et al., 2010) and evaluate mobile/less-mobile porosity exchange occurring in shallow sediments (Briggs et al., 2018).

However, this strong dependence of DC electrical conductivity on pore fluid electrical conductivity limits its use for quantifying variations in sediment physical properties in dynamic streambed settings where substantial spatiotemporal changes in pore fluid electrical conductivity often occur. In addition, the electrical conductivity measured with DC resistivity in a streambed setting is strongly influenced by the surface water layer (thickness and electrical conductivity), complicating data interpretation (Day-Lewis et al. 2006).

The low-frequency ($f < 100$ Hz) alternating current method, complex electrical conductivity (CC) (also known as spectral induced polarization (SIP)), extends the information on electrical properties measurable with DC resistivity methods to include electrical charge storage (Kemna et al. 2012). The real component of CC describes electrical current conduction as measured with the DC resistivity method. The imaginary component additionally measured with CC results from electrical charge displacement in the electrical double layer (EDL) surrounding sediment grains, which is only weakly dependent on the pore fluid conductivity (an exception is in the presence of strong electronically conducting materials like pyrite and magnetite) (Vinegar & Waxman 1984). Imaginary conductivity is primarily a function of sediment physical properties, including
surface area (Börner & Schön 1991), grain size (Revil & Florsch, 2010), and CEC (Vinegar & Waxman 1984). Consequently, the CC method has been applied for mapping changes in lithology (e.g., Slater & Lesmes, 2002), estimating hydraulic conductivity (e.g., Binley et al., 2005), and imaging microbial-induced mineral precipitation (Saneiyan et al. 2019). While a time-domain form of CC has been applied in a water environment (Benoit et al., 2018; Slater et al., 2010), no studies have yet attempted to utilize CC to evaluate the physical properties of dynamic, shallow (< 10 cm depth) streambed interface sediments where important biogeochemical reactions impacting river corridor water quality are concentrated (Findlay, 1995).

One potential application of streambed CC measurements is mapping the precipitation of Fe(III) oxides or hydroxides (referred to as Fe(III) oxides, e.g., ferrihydrite, goethite, hematite) associated with anoxic groundwater discharges resulting from contamination or enhanced biogeochemical reactions (Boano et al. 2014). These Fe(III) oxides are generated in shallow streambed interface sediments where anoxic groundwater containing high concentrations of dissolved Fe(II) ions mixes with oxygenated surface water. Streambed precipitation of Fe(III) oxides is observed downstream of discharges of leachate from both mine tailings (Gandy et al. 2007) and landfills (Bakyayita et al. 2019). Fe(III) oxides are also precipitated at anoxic discharge zones resulting from natural processes, including those associated with floodplain beaver ponds (Briggs et al., 2019). Rapid, non-invasive characterization of Fe(III) oxide distributions would aid identification of anoxic groundwater discharge zones associated with such processes and could enhance understanding of contaminant transport through river corridors where high surface area
Fe(III) oxides function as sorption sinks for a range of stream water contaminants (e.g., arsenic, uranium) (C. Fuller & Harvey 2000, Gandy et al. 2007). Fe(III) oxides are strong potential targets for CC mapping as the imaginary conductivity increases with sediment surface area (Weller et al., 2010); the surface area of natural goethite and ferrihydrite reaches 200 and 400 m² g⁻¹, respectively (Cornell & Schwertmann, 2003).

We explore the merit of applying four-electrode CC measurements at the streambed-stream water interface to characterize the physical properties of shallow streambed interface sediments in situ. After providing a background to CC, we present laboratory studies to demonstrate the controls of sediment properties on various CC parameters. We then use synthetic modeling to investigate the influence of the surface water layer on streambed CC measurements, a notorious complicating factor impacting more oft-used streambed electrical resistivity surveys. Finally, we illustrate the concept in the field by making measurements over anoxic groundwater discharge zones along a landfill-impacted coastal stream where fine-grained Fe(III) oxides are precipitated in shallow streambed sediments.

5.2 Complex conductivity of streambed interface sediments

A shallow streambed system can be depicted as a fully saturated sediment medium overlain by a stream water layer (Figure 5.1a). At low frequencies (f <100 Hz), the stream water does not support electrical charge storage and only conducts current, which is quantified by a DC electrical conductivity (σw). In contrast, the streambed sediments both conduct and store electrical charge, which is quantified as a CC (σ̃_{sed}, superscript * represents a complex number here).
\[\sigma_{\text{sed}}^*(\omega) = |\sigma_{\text{sed}}^*(\omega)|e^{j\phi_{\text{sed}}(\omega)} = \sigma_{\text{sed}}'(\omega) + \sigma_{\text{sed}}''(\omega)i = \]
\[|\sigma_{\text{sed}}^*(\omega)|\cos[\phi_{\text{sed}}(\omega)] + |\sigma_{\text{sed}}^*(\omega)|\sin[\phi_{\text{sed}}(\omega)]i,\]

where \(\omega\) is the angular frequency indicating the frequency dependence of the CC parameters (we mainly focus on interpretation of single frequency data and do not include \(\omega\) in later symbols for simplicity). \(|\sigma_{\text{sed}}^*|\) is the magnitude of the CC, \(\phi_{\text{sed}}\) is the phase, \(i\) is the imaginary unit where \(i = \sqrt{-1}\) and \(\sigma'_{\text{sed}}\) and \(\sigma''_{\text{sed}}\) are the streambed real and imaginary conductivity, respectively.

Figure 5.1 Illustration of streambed CC measurement and CC theory. (a). Schematic diagram of CC measurement based on a simplified shallow streambed system with electrical conduction through both water and sediment layers, and polarization only in the sediment layer; four electrodes A, B, N and M are placed at the streambed-stream water interface to acquire the CC data; example electrode layout based on a dipole-dipole array; (b). Conceptual diagram of charge transport mechanisms in fully saturated porous sediments; electrolytic (\(\sigma_{\text{el}}\)) and surface (\(\sigma_{\text{surf}}\)) conduction act in parallel, whereas measured sediment polarization (\(\sigma_{\text{sed}}''\)) depends only on \(\sigma_{\text{surf}}''\); the two conceptual subplots highlight
that $\sigma_{\text{sed}}$ is strongly dependent on pore fluid conductivity $\sigma_I$ (Eq. 5.3), while $\sigma_{\text{sed}}'\text{sed}$ is strongly dependent on specific surface area $S_m$ (Eq. 5.8) and only weakly dependent on $\sigma_I$ (c). Principle of complex impedance measurement ($Z_{\text{meas}}$) from sinusoidal current (amplitude $|I|$) and voltage (amplitude $|\Delta U|$) at frequency $f$; $|Z_{\text{meas}}|$ is the measured impedance magnitude and $\phi_{\text{meas}}$ is the measured phase as discussed later in Section 5.3.2.

In Eq. (5.1), $\sigma_{\text{sed}}'$ includes a contribution from electrolytic conduction via the fluids in the interconnected pore space ($\sigma_{el}$) and a contribution from surface conduction at the sediment-fluid interface ($\sigma_{\text{surf}}'$). In contrast, $\sigma_{\text{sed}}''$ exclusively results from the polarization of the sediment-fluid interfaces ($\sigma_{\text{surf}}''$). Assuming $\sigma_{el}$ and $\sigma_{\text{surf}}$ add in parallel (e.g., Vinegar & Waxman, 1984 and Figure 5.1b),

$$\sigma_{\text{sed}}^* = (\sigma_{el} + \sigma_{\text{surf}}') + \sigma_{\text{surf}}''i,$$

$$\sigma_{\text{sed}}' = \sigma_{el} + \sigma_{\text{surf}}' = \frac{1}{F}\sigma_I + \sigma_{\text{surf}}',$$

$$\sigma_{\text{sed}}'' = \sigma_{\text{surf}}'',$$

where $\sigma_I$ is the pore fluid electrical conductivity. The electrical formation factor ($F$) is related to the interconnected porosity $\varphi$ and a cementation exponent $m$ that depends on the tortuosity (or connectedness) of the pore network (Archie 1942).

$$F = \varphi^{-m}$$

Eq. (5.3) indicates the inherent ambiguity of $\sigma_{\text{sed}}'$ interpretation containing two conductivity terms. In cases where $\sigma_{\text{surf}}'$ is insignificant, variations in $\sigma_{\text{sed}}'$ (and hence $|\sigma_{\text{sed}}^*|$) often reflect variations in $\sigma_I$, being the basis for using DC resistivity and electromagnetic methods to investigate groundwater-surface water exchange (Cardenas & Markowski, 2011; Slater et al., 2010; Viezzoli et al., 2010). In contrast, $\sigma_{\text{sed}}''$ is foremost controlled by the physical properties of the porous matrix, with previous studies showing its direct correlation with
specific surface area, CEC and grain size (e.g., Slater & Glaser, 2003; Weller et al., 2010, Revil 2012). CC therefore has the potential to infer variations in physical properties of streambed sediments from variations in $\sigma''_{\text{sed}}$, thereby reducing the inherent uncertainty associated with the interpretation of DC resistivity or electromagnetic methods caused by their strong dependence on $\sigma_I$.

Here we consider sediments in the absence of strong electronically conducting minerals. Mechanistic and empirical models have been developed to establish quantitative, predictive relationships between $\sigma''_{\text{sed}}$ and the physical properties of sediments (e.g., Leroy et al., 2008; Revil, 2012; Weller & Slater, 2015; Weller et al., 2010). Vinegar & Waxman (1984) proposed a semi-empirical model describing $\sigma''_{\text{sed}}$ of shaly sands as a function of excess charge per unit pore volume ($Q_v$, in C m$^{-3}$), a parameter related to CEC (in C kg$^{-1}$),

$$\sigma''_{\text{sed}} \approx \frac{1}{F\varphi} \frac{\lambda Q_v}{\lambda \rho_g} \frac{1 - \varphi}{\varphi} \text{ CEC},$$  \hspace{1cm} (5.6)

where $\lambda$ is the equivalent conductance, being a fitted empirical parameter. Revil (2012) and Revil (2013) developed a mechanistic model for clayey sands that describes the dependence of $\sigma''_{\text{sed}}$ on the electrochemical properties of the Stern (fixed) layer of the EDL,

$$\sigma''_{\text{sed}} \approx \frac{1}{F\varphi} \beta_s f_s \rho_g \text{ CEC},$$  \hspace{1cm} (5.7)

where $\beta_s$ is the mobility of counterions in the Stern layer, $f_s$ is the counterion fraction in the Stern layer ($1 - f_s$ is the counterion fraction in the diffuse layer) and $\rho_g$ is the grain density. As the specific surface area ($S_m$) is equivalent to the CEC divided by the charge density per unit surface area ($Q_s$),
\[
\sigma''_{\text{sed}} \approx \frac{1}{F\varphi} \beta_s f_s Q_s \rho_g S_{\text{m}} \approx a_p S_{\text{m}}. 
\] (5.8)

Assuming that \(\beta_s, f_s, Q_s\) are constant (valid for a limited range of \(\sigma_t\)), \(\rho_g\) is constant, and \(F\varphi\) exhibit only small variations, Eq. (5.8) predicts a linear dependence of \(\sigma''_{\text{sed}}\) on \(S_{\text{m}}\) with a slope of \(a_p\). This linear relationship has been observed in laboratory experiments (e.g., Börner & Schon, 1991). However, observations from a large experimental database of sandstones and unconsolidated sediments (from clean sands to clay-sand mixtures) suggest that \(\sigma''_{\text{sed}}\) is foremost controlled by the specific surface area normalized to the pore volume, \(S_{\text{por}}\) (Weller et al., 2010),

\[
S_{\text{por}} = \rho_g \frac{1 - \varphi}{\varphi} S_{\text{m}}. 
\] (5.9)

By substituting Eq. (5.9) into Eq. (5.8),

\[
\sigma''_{\text{sed}} \approx \frac{1}{F(1 - \varphi)} \beta_s f_s Q_s S_{\text{por}} \approx c_p S_{\text{por}}, 
\] (5.10)

where \(c_p\) is the specific polarizability, which Weller et al. (2010) assumed foremost reflects the role of the EDL chemistry on the polarization. This assumption relies on the investigated samples having a relatively small variation in \(F\) (Börner, 1992; Börner et al., 1996; Weller & Slater, 2012, 2019). When samples extend across a wide range of materials to include low permeability samples with high \(F\), then a more correct correlation separating out the role of the pore geometry from the EDL chemistry is (Niu et al., 2016; Weller & Slater, 2012, 2019),

\[
\sigma''_{\text{sed}} \approx c_q \frac{S_{\text{por}}}{F}, 
\] (5.11)
where \( c_q \) is a specific polarizability related only to the EDL chemistry (assuming a relatively narrow range of \((1-\varphi)\) in Eq. (5.10)).

Although Eqs. (5.7-5.11) are built from an initial model for shaly sandstones, they have been used (sometimes with slight modifications) to describe \( \sigma''_{sed} \) in a wide range of porous materials, including unconsolidated sediments (Revil, 2012) and soils (Revil et al., 2017). Our focus is shallow streambed sediments primarily composed of unconsolidated sandy materials characterized by relatively high porosity \( \varphi \) and low formation factor \( F \). Consequently, in our study we expect that the surface area terms (\( S_m, S_{por} \)) exert the dominant control on \( \sigma''_{sed} \). We demonstrate how this results in strong sensitivity to the precipitation of high surface area Fe(III) oxides due to groundwater discharge in the shallow streambed.

### 5.3 Methods

The study was performed on a groundwater-fed glacial coastal stream—Mashpee River in Massachusetts, USA. Anoxic groundwater discharge is associated with leachate from an upgradient landfill (Colman et al., 2004; Massachusetts Bureau of Resource Protection, 2006), resulting in rust-stained streambed sediments indicative of relatively high concentrations of Fe(III) oxides (Figures 5.2a). To investigate the dependence of \( \sigma''_{sed} \) on variations in streambed sediment properties associated with these discharge zones, laboratory CC measurements coupled with sediment Fe(III) and specific surface area analyses were first performed using sampled sediments from the Mashpee River. Field in situ CC measurements were then performed along the river. An analytical model was
developed to explore the effects of a variable water layer on the determination of $\sigma_{\text{sed}}^*$ from such in situ streambed CC measurements.

Figure 5.2 Streambed sediment samples and CC measurements. (a) Examples of dried streambed sediments for laboratory analyses with enhanced rust color from left to right due to increasing concentration of Fe(III) oxides; (b). Example of raw measured impedance magnitude $|Z_{\text{meas}}|$ and measured phase $\phi_{\text{meas}}$ spectra from laboratory CC measurements on sediments containing Fe(III) oxides; (c) Photo of field streambed CC measurement set-up; (d). Example of raw measured impedance magnitude $|Z_{\text{meas}}|$ and measured phase $\phi_{\text{meas}}$ from field in situ CC measurements in the Mashpee River.

### 5.3.1 Laboratory measurements

Surficial (0-5 cm depth) streambed sediments were sampled using a plastic scoop shovel at various locations along the Mashpee River. To make the samples consistent across various analyses, all sediments were dried and sieved to exclude small fractions of large particles (>2 mm). This was done to reduce analysis bias that would occur when incorporating large grains as the sample volumes used for Fe(III) and surface area analyses
were necessarily small (< 8 mL). Laboratory CC measurements were performed by saturating and packing the sediments into an acrylic cylindrical four-electrode column following a design and procedure described in Wang and Slater (2019). The sediments were first saturated using stream water (conductivity of 110 μS cm⁻¹) in a glass beaker and then packed in a wet state by gradual addition of sediment to the column. To achieve a fully saturated sample packing, a small volume of stream water was added to the column followed by the addition of a small volume of wet sediments, with the process completed until columns were filled. During the packing process, the column was frequently placed on a sieve shaker to vibrate air bubbles out of the sediments and promote uniform packing.

The CC data from 0.1 to 100 Hz were measured with a Portable Spectral Induced Polarization instrument (PSIP, Ontash & Ermac Inc., NJ, USA). Figure 5.2b shows an example of raw CC spectra of sediment containing Fe(III) oxides. The spectra show a relatively low frequency dependence with measured phase ranging from -5 to -11 mrad. After each measurement, the pore fluids were collected by pushing the pore fluid out of the column using a syringe. Pore fluid conductivity was then measured after passing the fluids through a 0.45 μm filter to avoid the influence of charged suspended particulates on the conductivity readings. Pore fluid conductivity varied from 146 to 838 μS cm⁻¹ due to varying degrees of redox activity and ion dissolution during wet sample storage before drying. The packed sediment porosity was determined by weighing the water loss after drying a fully saturated sample in an 80 °C oven for 24 hrs.
Sediment specific surface area was measured using the Brunauer-Emmett-Teller (BET) nitrogen gas adsorption method (Brunauer et al. 1938). Sediment Fe(III) concentration was determined spectrophotometrically by the ferrozine method (Stookey 1970). Dry sediments of ≈1 g were digested in 2 mL 6M hydrochloric acid for one week to dissolve Fe(III) oxides. The concentration of Fe(II) and total Fe (with all the Fe(III) reduced to Fe(II) by hydroxylamine hydrochloride) in the acid digest was determined by measuring the absorbance of colored Fe(II) complex of ferrozine at 562 nm. Fe(III) concentration in the digest was calculated by subtraction of Fe(II) from total Fe and then converted to dry sediment concentration in mg g$^{-1}$ given the known sediment weight and liquid volume.

5.3.2 Analytical model and synthetic study

Numerical methods are now routinely used to model and invert electrical geophysical datasets acquired using 2D or 3D arrays of electrodes placed on the Earth surface or in boreholes. These methods provide estimates of the 2D or 3D distribution of the electrical properties of the subsurface over the region encompassed by the electrodes. However, our objective is to precisely determine the sediment CC within a shallow support volume (upper 10 cm) of a single four-electrode measurement made on the streambed from a measured apparent CC that is a function of the electrical properties of both the sediments and the water layer. This inverse problem has an analytical solution, which is preferred for ease of implementation, for example direct computation in the field. However, we also compare the analytical solution against a numerical solution obtained using COMSOL Multiphysics®. The key findings of our modeling apply equally to more complex 2D and 3D numerical models.
The principle of a streambed CC measurement using the dipole-dipole array is illustrated in Figure 5.1a. The dipole-dipole array is a common choice in induced polarization surveys as separating the current and potential dipoles reduces electromagnetic coupling errors (Ward, 1988; Zonge et al., 2005). A sine wave source injects current $\tilde{I}$ between a pair of point electrodes A and B while the potential difference ($\Delta \tilde{U}$) is measured between another pair of point electrodes M and N. According to Ohm’s law, the measured complex electrical impedance $Z_{\text{meas}}^*$ (recorded as a measured magnitude $|Z_{\text{meas}}^*|$ and measured phase $\phi_{\text{meas}}$ by a CC instrument, Figure 5.1c) is given by,

$$Z_{\text{meas}}^* = |Z_{\text{meas}}^*| e^{\phi_{\text{meas}} i} = \frac{\Delta \tilde{U}}{\tilde{I}} = \frac{(\tilde{U}_{AM} - \tilde{U}_{BM}) - (\tilde{U}_{AN} - \tilde{U}_{BN})}{\tilde{I}}, \quad (5.12)$$

where $\tilde{U}_{AM}$, $\tilde{U}_{BM}$, $\tilde{U}_{AN}$ or $\tilde{U}_{BN}$ are the potentials at electrodes M or N contributed from the positive current source A or the negative current source B. All the voltage and current terms in Eq. (5.12) are sine functions, which results in a complex number $Z_{\text{meas}}^*$. The relationship between each potential term $\tilde{U}_x$ (where $x$ is either $\text{AM}$, $\text{BM}$, $\text{AN}$ or $\text{BN}$) and $\tilde{I}$ can be derived from an extension of the method of images (Keller & Frischknecht, 1966) to complex electrical properties. The method of images accounts for the electrical current reflections from the water-streambed and water-air boundaries (derivation in Appendix C),

$$\frac{\tilde{U}_x}{\tilde{I}} = \frac{1}{4\pi r_x \sigma_w} \left[ 1 + k_{w,\text{sed}}^* + \sum_{n=1}^{\infty} \frac{(k_{w,\text{sed}}^*)^{n-1}(k_{w,\text{sed}}^* + 1)^2}{\sqrt{1 + [2n(d/r_x)]^2}} \right], \quad (5.13)$$

where $r_x$ is the distance between the corresponding current and potential electrode, $d$ is the water depth and $k_{w,\text{sed}}^*$ is the complex conductivity reflection coefficient,
\[ k_{w,\text{sed}}^* = \frac{\sigma_w - \sigma_{\text{sed}}^*}{\sigma_w + \sigma_{\text{sed}}^*} \quad (5.14) \]

Eq. (5.13) is derived with the assumptions of point current/potential electrodes at the water-streambed interface and constant water layer depth and conductivity within the range of measurement sensitivity. By substituting Eq. (5.13) into each potential term in Eq. (5.12), \( \sigma_{\text{sed}}^* \) can be inverted with known \( Z_{\text{meas}}^* \), \( r_x \), \( d \) and \( \sigma_w \) (using a large enough value of \( n \) (e.g., 100) will ensure a good approximation of the convergent series). The scipy.optimize module in python (Virtanen et al. 2020) was used for the computation.

To assess the influence of the water layer on the CC terms, \( Z_{\text{meas}}^* \) was determined for the synthetic model shown in Figure 5.1a using representative conductivity values for a freshwater streambed system. The sediment \( \sigma_{\text{sed}}^* \) was fixed to have \( \sigma'_{\text{sed}} = 25 \mu S \text{ cm}^{-1} \) and \( \sigma''_{\text{sed}} = 0.5 \mu S \text{ cm}^{-1} \) (\( \phi_{\text{sed}} = 20 \text{ mrad} \)). A water layer with \( \sigma_w \) set as either 50, 100 or 150 \( \mu S \text{ cm}^{-1} \), was modeled to account for different contrasts between \( \sigma_w \) and \( \sigma'_{\text{sed}} \), i.e., \( \sigma_w/\sigma'_{\text{sed}} = 2 \), 4 and 6, respectively. The electrodes were equally spaced. The total distance of the four-electrode array (i.e., distance between electrodes A and M in Figure 5.1a) is defined as the maximum electrode distance \( r_{\text{max}} \). For each \( \sigma_{\text{sed}}^*-\sigma_w \) combination, \( Z_{\text{meas}}^* \) was computed with \( d/r_{\text{max}} \) ranging from \( 5 \times 10^{-4} \) to 50, spanning a range from negligible to approximating infinite \( d \) relative to \( r_{\text{max}} \). \( Z_{\text{meas}}^* \) can be transformed to an apparent CC (\( \sigma_{\text{app}}^* \)) by multiplying by the geometric factor for a four-electrode array located at the surface of a half-space,

\[ \sigma_{\text{app}}^* = \frac{1}{2\pi Z_{\text{meas}}^*} \left[ \left( \frac{1}{r_{\text{AM}}} - \frac{1}{r_{\text{BM}}} \right) - \left( \frac{1}{r_{\text{AN}}} - \frac{1}{r_{\text{BN}}} \right) \right], \quad (5.15) \]
which represents the CC of an equivalent homogeneous, isotropic half-space in the absence of the water layer. The relationship between $\sigma_{\text{app}}^*$ and $\sigma_{\text{sed}}^*$ was established by combining Eqs. (5.12-5.15), which has two limits: (1) when $dl/r_{\text{max}} \to 0$, i.e., the water layer is very shallow and negligible compared to the electrode range, $\sigma_{\text{app}}^* = \sigma_{\text{sed}}^*$ and (2) when $dl/r_{\text{max}} \to +\infty$, i.e., the water layer is very deep and can be approximated as infinite relative to the electrode separation, $\sigma_{\text{app}}^* = \sigma_{\text{sed}}^* + \sigma_w$, meaning a parallel addition of conduction in the two media,

$$\sigma_{\text{app}}' = \sigma_{\text{sed}}' + \sigma_w = \sigma_{\text{sed}}' \left(1 + \frac{\sigma_w}{\sigma_{\text{sed}}'}\right), \quad (5.16)$$

$$\phi_{\text{app}} = \phi_{\text{sed}} \frac{1}{\left(1 + \frac{\sigma_w}{\sigma_{\text{sed}}'}\right)}, \quad (5.17)$$

$$\sigma_{\text{app}}'' = \sigma_{\text{sed}}'', \quad (5.18)$$

Eqs. (5.16-5.18) explicitly show the influence of a very deep water layer on $\sigma_{\text{app}}^*$, where $\sigma_{\text{app}}'$ overestimates $\sigma_{\text{sed}}'$, $\phi_{\text{app}}$ underestimates $\phi_{\text{sed}}$ and $\sigma_{\text{app}}''$ is a direct measure of $\sigma_{\text{sed}}''$.

Inverse modeling was performed using the synthetic values of $Z_{\text{meas}}$ computed above. Model parameters $d$ and $\sigma_w$ were assigned ±5% errors to explore the sensitivity of inverted $\sigma_{\text{sed}}'$ to uncertain field measurements of these parameters, which will be enhanced by more turbulent streamflow.

### 5.3.3 Field experiments

In situ streambed CC measurements were performed at discrete locations in the Mashpee River channel. Each measurement was made using a dipole-dipole array by placing a four-electrode probe at a flat location on the water-streambed interface to match the scenario
illustrated in Figure 5.1a. The probe was constructed by wrapping four 1-cm-wide Ag-AgCl strips spaced 14 cm apart onto a plastic rod (i.e., total array length for four electrodes is 42 cm) (Figure 5.2c). The relatively small electrode spacing focuses sensitivity on the region of the shallow streambed where Fe(III) oxides precipitate due to high dissolved oxygen. The depth of investigation (DOI) of the probe was evaluated to range from 4 to 9 cm, decreasing with greater water depth, based on a DOI calculation method proposed by Oldenburg & Li (1999). The CC data from 0.1 to 100 Hz were collected using the same instrument as that used for laboratory measurements. Coaxial cables were used to connect the probe to the instrument. The entire set-up was carried and/or moved by a canoe in the river channel to take the measurements (Figure 5.2c). Figure 5.2d shows an example of a raw CC spectrum measured with the probe on the streambed. The shape of the spectrum is consistent with that measured in the laboratory (Figure 5.2b), although the curve appears slightly noisier. At each measurement location, water depth was recorded and assigned ±1 cm uncertainty, being partly attributed to variations in stream flow. The specific conductance (stream water conductivity at 25 °C) and temperature were recorded by a portable conductivity meter (Orion Star, Thermo Scientific), from which the actual stream water conductivity was calibrated with a linear coefficient of 2.1% / °C with a ±5% estimated uncertainty. $\sigma_{\text{sed}}^*$ and an associated uncertainty range were determined from measured $Z_{\text{meas}}$, $d$ and $\sigma_w$ using Eqs. (5.12-5.14).

5.4 Results

Results from laboratory, synthetic modeling and field studies are presented to demonstrate the characterization of streambed sediment properties using CC measurements.
5.4.1 Laboratory results

Laboratory analyses of CC and associated properties on the extracted sediment are summarized in Table 5.1. The sediment Fe(III) concentration ranges from 1.2 to 20.2 mg g\(^{-1}\) indicating various amounts of Fe(III) oxide precipitates produced by anoxic groundwater discharge in the Mashpee River. Given the relatively uniform texture of the sandy streambed sediment, the presence of fine-grained Fe(III) oxides explains most of the variations in specific surface area (Figure 5.3a). Using single frequency data at 4 Hz, laboratory-measured \(\sigma_{\text{sed}}''\) is significantly correlated with the specific surface area \(\left(R^2=0.87, p<0.05\right)\), being consistent with Eq. (5.8) (Figure 5.3b). Assuming a constant ratio of 0.042 between \(\sigma_{\text{sed}}''\) (i.e., \(\sigma_{\text{surf}}''\)) and \(\sigma_{\text{surf}}'\) (Weller et al., 2013), \(\sigma_{\text{surf}}'\) only accounts for 2% to 17% of \(\sigma_{\text{sed}}'\). Therefore, variations in \(\sigma_{\text{sed}}'\) mainly result from changes in \(\sigma_i\) (Figure 5.3d) as the porosity \(\varphi\) and formation factor \(F\) do not vary greatly in these unconsolidated materials (Table 5.1). In contrast, \(\sigma_{\text{sed}}''\) shows no dependence on \(\sigma_i\) (Figure 5.3c), further highlighting its value for mapping variations in physical properties of streambed sediments. The low impact of \(\sigma_i\) on \(\sigma_{\text{sed}}''\) can also be observed for the samples with triplicate measurements (samples M2, M5 and M7 in Table 5.1), in which \(\sigma_{\text{sed}}''\) varies less than 10% despite \(\sigma_i\) changing up to 90%. In such situations, \(\sigma_{\text{sed}}'\) shows no correlation with the specific surface area and cannot provide meaningful information on the sediment physical properties (Figure 5.3e).

Table 5.1 Summary of extracted Mashpee River sediment properties measured in the laboratory.
<table>
<thead>
<tr>
<th>NO.</th>
<th>Fe(III) (^a) (mg g(^{-1}))</th>
<th>(S_m) (m(^2) g(^{-1}))</th>
<th>(\varphi) (^b)</th>
<th>(\sigma_f) ((\mu)S cm(^{-1}))</th>
<th>(\sigma_{sed}^{(4\text{Hz})}) ((\mu)S cm(^{-1}))</th>
<th>(\sigma_{sed}^{(100\text{Hz})}) ((\mu)S cm(^{-1}))</th>
<th>(F) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>1.2±0.2</td>
<td>0.41</td>
<td>38.5%</td>
<td>253.5</td>
<td>61.5</td>
<td>0.048</td>
<td>0.089</td>
</tr>
<tr>
<td>M1</td>
<td>5.8±0.5</td>
<td>2.73</td>
<td>40.1%</td>
<td>316.5</td>
<td>76.9</td>
<td>0.069</td>
<td>0.174</td>
</tr>
<tr>
<td>M2</td>
<td>6.8±0.4</td>
<td>2.06</td>
<td>35.6%</td>
<td>372.1</td>
<td>66.9</td>
<td>0.051</td>
<td>0.102</td>
</tr>
<tr>
<td>M3</td>
<td>4.4±0.9</td>
<td>2.36</td>
<td>34.1%</td>
<td>160.5</td>
<td>33.9</td>
<td>0.057</td>
<td>0.077</td>
</tr>
<tr>
<td>M4</td>
<td>4.8±1.0</td>
<td>2.15</td>
<td>36.1%</td>
<td>NA</td>
<td>56.1</td>
<td>0.047</td>
<td>0.094</td>
</tr>
<tr>
<td>M5</td>
<td>8.7±1.2</td>
<td>3.96</td>
<td>39.3%</td>
<td>446.5</td>
<td>110.6</td>
<td>0.129</td>
<td>0.235</td>
</tr>
<tr>
<td>M6</td>
<td>15.5±2.0</td>
<td>4.56</td>
<td>34.7%</td>
<td>221.8</td>
<td>43.5</td>
<td>0.104</td>
<td>0.265</td>
</tr>
<tr>
<td>M7</td>
<td>14.3±0.1</td>
<td>5.67</td>
<td>34.3%</td>
<td>146.4</td>
<td>28.1</td>
<td>0.199</td>
<td>0.327</td>
</tr>
<tr>
<td>M8</td>
<td>20.2±2.4</td>
<td>5.30</td>
<td>36.0%</td>
<td>166.0</td>
<td>36.3</td>
<td>0.149</td>
<td>0.381</td>
</tr>
</tbody>
</table>

\(^a\) Three samples M2, M5 and M7 were packed in triplicate to evaluate uncertainties in CC measurements.

\(^b\) Data are mean ± standard deviation from triplicate of each sample.

\(^c\) The porosity \(\varphi\) has an uncertainty of ±0.5% determined from triplicate of samples M2, M5 and M7.

\(^c\) \(F\) was estimated using Eq. (5.3) assuming a constant ratio between \(\sigma_{surf}\) and \(\sigma_{sed}\):
\[
F = \frac{\sigma_f}{(\sigma_{sed}^{(4\text{Hz})} - \sigma_{sed}^{(100\text{Hz})})/0.042}
\]
(Weller et al., 2013)
Previous studies have proposed that it is $S_{por}$, or more correctly, $S_{por}/F$ that is the critical pore geometry term controlling $\sigma_{sed}''$ (e.g., Niu et al., 2016; Weller et al., 2010; Weller & Slater, 2012). In our case, the linear regression of $\sigma_{sed}''$ versus $S_{por}$ and $\sigma_{sed}''$ versus $S_{por}/F$ gives similar (or slightly lower) $R^2$ values to those obtained for the linear regression of $\sigma_{sed}''$ versus $S_m$ (Figure 5.4). This reflects the limited variability in $\phi$ and $F$ for the unconsolidated streambed samples studied here (Table 5.1). The laboratory $\sigma_{sed}''$ measured at 100 Hz shows a similar linear dependence on $S_m$, $S_{por}$ or $S_{por}/F$ to that observed for $\sigma_{sed}''$ at 4 Hz, although the relative change in $\sigma_{sed}''$ for a change in the pore geometry term (i.e., the slope of the line) is significantly larger (Figure 5.4). While our laboratory results are consistent with theory and previous studies, we observe a specific intrinsic control on specific surface area sensed.
with imaginary conductivity due to fine-grained Fe(III) oxides precipitates induced by anoxic groundwater discharges.

Figure 5.4 Correlations of laboratory $\sigma''_{\text{sed}}$ at two frequencies with surface area parameters for the Mashpee River sediments. (a) $\sigma''_{\text{sed}}$ versus $S_m$; (b) $\sigma''_{\text{sed}}$ versus $S_{\text{por}}$; (c) $\sigma''_{\text{sed}}$ versus $S_{\text{por}}/F$.

5.4.2 Synthetic modeling

For an in situ CC measurement as shown in Figure 5.1a, the presence of the water layer has a large impact on the data acquisition. Figure 5.5a presents the influence of the water layer on modeled apparent complex conductivity $\sigma^*_{\text{app}}$ (expressed as $\sigma'_{\text{app}}$, $\phi_{\text{app}}$ and $\sigma''_{\text{app}}$) for a dipole-dipole electrode configuration as shown in Figure 5.1a. With an increase in the ratio of water depth $d$ to the maximum electrode distance $r_{\text{max}}$ (i.e., distance between electrodes A and M), $\sigma^*_{\text{app}}$ can be separated into three regions: (I) $d/r_{\text{max}} < 0.01$, approximating negligible $d$, (II) $0.01 < d/r_{\text{max}} < 1$ and (III) $d/r_{\text{max}} > 1$, approximating an infinite $d$ condition. In Region I, each $\sigma^*_{\text{app}}$ parameter equals the corresponding sediment complex conductivity $\sigma^*_{\text{sed}}$ parameter (i.e., $\sigma'_{\text{sed}}$, $\phi_{\text{sed}}$ or $\sigma''_{\text{sed}}$) representing a negligible water layer impact. Increasing $d$ as well as the contrast between water conductivity $\sigma_w$ and $\sigma'_{\text{sed}}$ significantly increases $\sigma'_{\text{app}}$ and decreases $\phi_{\text{app}}$ as shown in Region II. In Region III, $\sigma'_{\text{app}}$
reaches a plateau $\sigma_w/\sigma_{\text{sed}}$ times larger than $\sigma_{\text{sed}}$ while $\phi_{\text{app}}$ reaches a plateau $\sigma_w/\sigma_{\text{sed}}$ times smaller than $\phi_{\text{sed}}$. In contrast, $\sigma''_{\text{app}}$ is only weakly affected by the water layer in Region II and is equal to $\sigma''_{\text{sed}}$ in Region III. For the three cases with $\sigma_w/\sigma_{\text{sed}} = 2, 4$ and $6$, the maximum difference ranges from 206% to 624% between $\sigma'_{\text{app}}$ and $\sigma'_{\text{sed}}$ and from 68% to 87% between $\phi_{\text{app}}$ and $\phi_{\text{sed}}$. The equivalent difference only ranges from 12% to 22% between $\sigma''_{\text{app}}$ and $\sigma''_{\text{sed}}$.

Numerical modeling using COMSOL Multiphysics® software provided identical results (markers in Figure 5.5a). Therefore $\sigma'_{\text{app}}$ will significantly overestimate $\sigma'_{\text{sed}}$ and underestimate $\phi_{\text{sed}}$ in the presence of a non-negligible water layer. However, an unexpected and important result of this modeling is that $\sigma''_{\text{app}}$ will directly provide a good estimate of $\sigma''_{\text{sed}}$ when $d$ and $\sigma_w$ are unavailable or uncertain. The same results are found for other commonly used electrode configurations (e.g., Wenner and Schlumberger array in Figure C.2 in Appendix C).

Figure 5.5 Synthetic modeling results for a homogeneous sediment layer with $\sigma'_{\text{sed}} = 25$ $\mu$S cm$^{-1}$ and $\sigma''_{\text{sed}} = 0.5$ $\mu$S cm$^{-1}$ ($\phi_{\text{sed}} = 20$ mrad) below a water layer with varying $d$ and $\sigma_w$. (a) Impacts of water layer on $\sigma_{\text{app}}$; Each curve shows three regions I, II and III based on the ratio of $d$ to $r_{\text{max}}$; The open circles are numerical calculations obtained using COMSOL
Multiphysics® for $\sigma_w = 100$ $\mu$S cm$^{-1}$; Dashed lines represent the true parameter values of the sediments. (b) Uncertainties of inverted $\sigma_{\text{sed}}^*$ given $\pm5\%$ errors on $d$ and $\sigma_w$; in each subplot, two curves of the same color represent the maximum and minimum of the inverted parameters for nine computations with varying relative errors in $d$ and $\sigma_w$, being either $0\%$, $-5\%$ or $+5\%$; Dashed lines represent the true parameter values of the sediments.

Although $\sigma_{\text{sed}}^*$ can be inverted with known $d$ and $\sigma_w$ of the water layer, the sensitivity of inverted $\sigma_{\text{sed}}^*$ to the uncertainties of input $d$ and $\sigma_w$ must be evaluated. Figure 5.5b presents the uncertainty range of inverted $\sigma_{\text{sed}}^*$ when adding $\pm5\%$ errors on $d$ and $\sigma_w$. These errors in $d$ and $\sigma_w$ cause larger errors in the inverted $\sigma_{\text{sed}}'$ (up to $48\%$) and $\phi_{\text{sed}}$ (up to $139\%$), and the errors increase with increasing $\sigma_w/\sigma_{\text{sed}}'$ ratio. For each $\sigma_w$ scenario, the maximum uncertainty exists in Region II due to the collective contributions from both $d$ and $\sigma_w$ errors. The maximum uncertainty ranges of $\sigma_{\text{sed}}'$ are $-15\%$ to $+15\%$, $-33\%$ to $+31\%$, and $-53\%$ to $+48\%$ for the models with $\sigma_w/\sigma_{\text{sed}}'$ equal to 2, 4 and 6, respectively. Similarly, $\phi_{\text{sed}}$ shows large uncertainties with maximum ranges $-14\%$ to $+19\%$, $-26\%$ to $+56\%$ and $-36\%$ to $+139\%$ at $\sigma_w/\sigma_{\text{sed}}' = 2$, 4 and 6, respectively. In Region III, the uncertainties of inverted $\sigma_{\text{sed}}'$ and $\phi_{\text{sed}}$ become independent of $d$, but still contains magnified errors associated with $\sigma_w$.

This highlights the difficulty of accurate determination of shallow streambed sediment or pore fluid properties using $\sigma_{\text{sed}}'$ as recorded with DC resistivity. In contrast, inverted $\sigma_{\text{sed}}''$ contains low errors (no more than $13\%$) in Region II, with maximum uncertainties limited to between $-1.2\%$ to $+1.2\%$, $-2.5\%$ to $+4.8\%$, and $-4.6\%$ to $+12.8\%$ for the model with $\sigma_w/\sigma_{\text{sed}}' = 2$, 4 and 6, respectively. As $\sigma_{\text{app}}''$ is equal to $\sigma_{\text{sed}}''$ in Region III, inverted $\sigma_{\text{sed}}''$ is independent of the water layer and therefore does not contain errors. In summary, these synthetic modeling results demonstrate the highly reduced sensitivity of $\sigma_{\text{sed}}''$ to the properties of the stream water layer compared to $\sigma_{\text{sed}}'$ and $\phi_{\text{sed}}$. 
5.4.3 **Field application of streambed CC measurements**

We compare the field acquired $\sigma_{\text{sed}}$ data from Mashpee River with the laboratory results and explore the spatial variations of $\sigma_{\text{sed}}^*$ along the Mashpee River in relation to the location of anoxic discharge zones.

5.4.3.1 **Evaluation of field data**

We compare inverted $\sigma_{\text{sed}}'$ and $\sigma_{\text{sed}}''$ spectra (0.1 to 100 Hz) acquired from field CC measurements with laboratory measurements on sediments taken from the same location. Figure 5.6 presents two sets of laboratory and field data collected from two different locations within the known Fe(III) oxide precipitation areas located in the Mashpee River. The higher uncertainties in field $\sigma_{\text{sed}}'$ relative to field $\sigma_{\text{sed}}''$ (error bars smaller than symbols) are expected given the synthetic modeling results described in Section 5.4.1. Both field and laboratory $\sigma_{\text{sed}}'$ are approximately frequency independent. Laboratory $\sigma_{\text{sed}}'$ values fall within the uncertainty range of field $\sigma_{\text{sed}}'$ measurements. Field $\sigma_{\text{sed}}''$ increases slightly with increasing frequency, being generally consistent with the shape of the laboratory spectra. Field $\sigma_{\text{sed}}''$ spectra contain some noise, particularly below 1 Hz (Figure 5.6a), which may reflect non-steady stream flow. In Figure 5.6a, field $\sigma_{\text{sed}}''$ between 1 to 20 Hz differs by less than 30% from the laboratory measurements. The increase of field $\sigma_{\text{sed}}''$ with increasing frequency above 20 Hz may result from the presence of fine particles that were lost during the sampling. In Figure 5.6b, the field $\sigma_{\text{sed}}''$ is 4-8 times higher than laboratory $\sigma_{\text{sed}}''$ between 0.1 to 100 Hz, although the frequency dependence is almost identical between field- and laboratory-measured $\sigma_{\text{sed}}''$. In general, the inverted estimates of field $\sigma_{\text{sed}}''$ provide spectra that are similar in shape to those determined from laboratory measurements. As with the
laboratory analysis, we focus on the interpretation of $\sigma_{\text{sed}}'$ and $\sigma_{\text{sed}}''$ at a single representative frequency of 4 Hz.

Figure 5.6 Comparison of $\sigma_{\text{sed}}'$ and $\sigma_{\text{sed}}''$ spectra between field (inverted) and laboratory measurements at two different locations (a) and (b) in Mashpee River. The error bars for $\sigma_{\text{sed}}'$ and $\sigma_{\text{sed}}''$ (smaller than the markers) are modeled parameter uncertainties based on assumed input uncertainties (i.e. ±5% for $\sigma_w$ and ± 1 cm for $d$).

5.4.3.2 Spatial variation of streambed CC

Figure 5.7a shows a segment of the Mashpee River passing a zone of Fe-rich anoxic groundwater discharge as evident by visible, rust colored, fine-grained streambed interface sediments. Elevated sediment Fe(III) concentration and specific surface area are observed towards the downstream end of the studied river reach (Figure 5.7b). The spatial variations of $\sigma_{\text{sed}}''$ (4 Hz) show a pattern consistent with sediment Fe(III) concentration and specific surface area variations, primarily reflecting the change in sediment properties due to anoxic
discharge associated with a landfill towards downstream areas (Figure 5.7). The model uncertainties for most $\sigma''_{sed}$ are less than 3%, indicating reliable measurements despite the input uncertainties. As demonstrated in the synthetic modeling, $\sigma''_{app}$ is found to be a good approximation of $\sigma''_{sed}$, making it possible to directly estimate $\sigma''_{sed}$ from the measurement even without knowledge of $\sigma_w$ and $d$ (Figure 5.7b). In contrast, $\sigma'_{app}$ is significantly larger than $\sigma'_{sed}$ as $\sigma'_{app}$ contains a large contribution from $\sigma_w$ (being 110 $\mu$S cm$^{-1}$). The large model uncertainties on $\sigma'_{sed}$ and the strong dependence of $\sigma'_{sed}$ on the pore fluid conductivity prevent a meaningful interpretation of this parameter to characterize sediment physical properties, which does not show any clear correspondence to downstream groundwater discharge locations.

Figure 5.7 Field streambed CC measurement results (at 4 Hz) for Mashpee River. (a) Survey area and spatial variations of $\sigma''_{sed}$ along the stream segment; groundwater table contours from Walter et al. (2019) (b) Laboratory-measured sediment Fe(III) concentration,
specific surface area ($S_m$) and in situ measured $\sigma''_{\text{sed}}$ and $\sigma'_{\text{sed}}$ variations from upstream to downstream; error bars for sediment Fe(III) are standard deviations from triplicate; errors bars for $\sigma''_{\text{sed}}$ (smaller than the markers) and $\sigma'_{\text{sed}}$ are modeled parameter uncertainties based on assumed input uncertainties (i.e. $\pm 5\%$ for $\sigma_w$ and $\pm 1\ cm$ for $d$). The background map is from Google Earth.

5.5 Discussion

We introduced a novel application of CC measurements on the streambed to map spatial variations in the physical properties of shallow streambed sediments. Implications from laboratory, synthetic modeling and field results are discussed below.

5.5.1 Laboratory relationship between imaginary conductivity and Fe(III) oxides

Laboratory measurements confirm the petrophysical relationship between CC parameters and physical properties of streambed sediments. The relatively low phase and imaginary conductivity responses along with the absence of pronounced peaks in the frequency spectra (Figures 5.2 and 5.6), suggest that the polarization of the fine-grained Fe(III) oxides is characteristic of the EDL polarization observed for non-electronically conducting materials. This is consistent with findings of Abdel Aal et al. (2014), who compared the polarization of various types of bulk Fe minerals, finding that hematite and goethite exhibit much weaker polarization signals than the electronic-conducting minerals pyrite and magnetite. We found a strong correlation between $\sigma''_{\text{sed}}$ and specific surface area $S_m$, where surface area is proportional to Fe(III) concentration (Figure 5.3). Previous petrophysical relationships were mostly established using databases composed of samples where physical properties (e.g., $S_m$, $S_{\text{por}}$, or $F$) vary over several orders of magnitude (e.g., Niu et al., 2016; Revil, 2013; Weller et al., 2010). Despite the narrow $S_m$ range in our samples, we still
observe a strong correlation between $\sigma''_{\text{sed}}$ and $S_m$, highlighting the opportunity to use CC measurements to characterize spatial variations in streambed physical properties.

The slopes of the $\sigma''_{\text{sed}}$-$S_m$ relation ($a_p$ in Eq. 5.8) and the $\sigma''_{\text{sed}}$-$S_{\text{por}}$ relation ($c_p$ in Eq. 5.10) using $\sigma''_{\text{sed}}$ at 4 Hz are determined to be $3.1 \times 10^{-9}$ S kg m$^{-3}$ and $6.5 \times 10^{-13}$ S, respectively (Figure 5.4). Both coefficients are about one order of magnitude smaller than those reported in previous studies for sand and clay minerals, e.g., $a_p = 7.6 \times 10^{-8}$ S kg m$^{-3}$ in Revil (2012) and $c_p = 5.6-24 \times 10^{-12}$ S in Weller et al. (2015). As the polarization of fine particles is enhanced at high frequencies, increased slopes are obtained using 100 Hz $\sigma''_{\text{sed}}$ data, giving $a_p$ (100 Hz) = $6.1 \times 10^{-9}$ S kg m$^{-3}$ and $c_p$ (100 Hz) = $1.3 \times 10^{-12}$ S (Figure 5.4). However, these coefficients are still significantly lower than previously reported values. The relatively low values of $a_p$ and $c_p$ might reflect a reduced charge density $Q_s$ in Eq. (5.8) and (5.10) resulting from the different EDL properties of Fe(III) oxides compared to that of sand and clay materials. For sand and clay minerals, the point of zero charge is around pH 3, resulting in net negatively charged grain surface charges attracting cations in fluids at pH 7 (stream water pH in this study) (Glover 2015). Although synthetic pure Fe(III) oxides have a point of zero charge in the pH range 7.5-9.5, natural Fe(III) oxides normally have a point of zero charge in the pH range 4-7 due to ion adsorption (Schwertmann & Fechter 1982, Cornell & Schwertmann 2003). The proximity of the stream water pH to the natural Fe(III) oxide point of zero charge may result in a low net $Q_s$ on Fe(III) oxides. While $Q_s$ is one parameter controlling the dependence of $\sigma''_{\text{sed}}$ on the surface area, $\beta_s$, $f_s$ in Eq. (5.8) and (5.10) are other factors that may differ for Fe(III) oxides relative to sand and clay minerals.
5.5.2 Effects of water layer on streambed CC measurements

Synthetic modeling illustrates the impact of the water layer on CC measurements made at the stream water-streambed interface. We found that $\sigma_{\text{sed}}^\prime$ can be determined accurately despite uncertainties in the water layer depth and electrical conductivity (Figure 5.5b). In contrast, $\sigma_{\text{sed}}^\prime$ and $\phi_{\text{sed}}$ will have high errors if the water layer is not accurately defined (e.g., 5% errors in depth $d$ and electrical conductivity $\sigma_w$). Considering how the CC measurement uncertainties driven by errors in $d$ and $r_{\text{max}}$ vary with the ratio $d/r_{\text{max}}$ (Figure 5.5b), electrode spacings that fall within Region II should be avoided. Although we only present three modeling examples with fixed $\sigma_{\text{sed}}^\ast$ ($\sigma_{\text{sed}}^\prime = 25 \mu S \text{ cm}^{-1}$ and $\sigma_{\text{sed}}^\prime = 0.5 \mu S \text{ cm}^{-1}$) and $\sigma_w = 50$, 100 or 150 $\mu S \text{ cm}^{-1}$, other cases with a similar ratio of $\sigma_w/\sigma_{\text{sed}}^\prime$ will give similar results as $\sigma_w/\sigma_{\text{sed}}^\prime$ determines the relative change of the curves in Figure 5.5 according to Eqs. (5.12-5.15). For a shallow streambed sediment composed of unconsolidated sediments, the pore water conductivity and hence $\sigma_{\text{sed}}^\prime$ is highly impacted by $\sigma_w$. Modeled scenarios with $\sigma_w/\sigma_{\text{sed}}^\prime = 2, 4$ or 6 in this study are considered representative of most freshwater shallow streambed systems.

In this study, we modeled a homogeneous subsurface within the support volume of the probe designed for shallow streambed sediment characterization. However, our findings are equally relevant to 2D or 3D numerical modeling and are consistent with previous 2D resistivity imaging, where incorrect $\sigma_w$ and $d$ estimates significantly degraded inversion results (Day-Lewis et al. 2006, Henderson et al. 2010) and resulted in inversion errors that increase with increasing $\sigma_w/\sigma_{\text{sed}}^\prime$ (Orlando 2013). We anticipate that images of $\sigma_{\text{sed}}^\prime$ from CC inversions will similarly have low uncertainties (relative to $\sigma_{\text{sed}}^\prime$ and $\phi_{\text{sed}}$ images) when
applied to a streambed or other water bottom environments. In addition, caution will be needed if inverting $\sigma'_{\text{sed}}$ and $\phi_{\text{sed}}$ from data acquired using electrode spacings with $dl/r_{\text{max}}$ falling in Region II due to the larger uncertainties.

5.5.3 Comparison between laboratory and field measurements

While we rely on the laboratory data to confirm the dependence of $\sigma''_{\text{sed}}$ on Fe(III) oxide concentrations, we examine the sensitivity of field data to the location of Fe(III) oxide precipitation zones. In Figure 5.7, we observe a generally consistent trend between $\sigma''_{\text{sed}}$ and Fe(III) concentration. However, some downstream locations with high Fe(III) concentration show low $\sigma''_{\text{sed}}$. This mismatch between $\sigma''_{\text{sed}}$ and Fe(III) concentration may result from the fact that $\sigma''_{\text{sed}}$ measures a relatively large volume of sediment (sensed by a 42-cm-long probe) whereas Fe(III) concentration was determined from only a small mass ($\sim 1$ g) of sampled surface sediment. The field data represent the bulk responses from a relatively large volume of sediment, whereas the laboratory data were acquired on a smaller volume of sampled sediments, which may not be entirely representative of the materials within the field-measured bulk volume. The groundwater discharge patterns in Mashpee River may be patchy instead of continuous, as reported in nearby Quashnet River within the same groundwater system and similar geological setting (Rosenberry et al. 2016, Walter et al. 2019). Besides, Fe(III) oxides are precipitated at a distinct redox interface. Therefore, the Fe(III) oxides may not be uniformly distributed within a wide range of sediments, possibly resulting in low average concentrations sensed as low field $\sigma''_{\text{sed}}$ responses. The different measurement scales also explain why field $\sigma''_{\text{sed}}$ data do not always match the laboratory-measured $\sigma''_{\text{sed}}$ (Figure 5.6b). In addition, packing/compaction may be
different between the materials sensed with the laboratory and field CC measurements, especially given the difficulty in repacking streambed sediments to exactly represent in situ conditions. We argue that these differences do not foremost reflect limitations of the field measurements; instead, they indicate that laboratory measurements on disturbed soils have limited applicability for characterization of in situ sediment properties. This highlights a critical need for in situ measurements of the streambed interface as laboratory measurements on sampled sediments will never be fully representative of true field conditions and scales. However, the measurement volume sensed with the field probe must be fully considered to provide a better understanding of the spatial variability of the sediment properties.

5.5.4 *In situ mapping of sediment properties using streambed CC measurements*

Our selected field study highlights one specific application of CC, being a rapid, non-invasive technology for identifying anoxic groundwater discharge zones resulting in high concentrations of Fe(III) oxides, especially when Fe(III) oxides are not visible due to deep or turbid water, aquatic vegetation, or shallow burial. These discharge zones can occur frequently when the groundwater is impacted by anthropogenic contamination such as landfill leachate (Bakyayita *et al.* 2019) and mining activities (Gandy *et al.* 2007) or natural processes such as beaver activity (Briggs *et al.* 2019) and organic-rich peat deposits (Briggs, *et al.*, 2018). Those processes consume the groundwater dissolved oxygen and increase the dissolved ions either by direct inputs or reducing the aquifer geological minerals, which result in unique discharge zones considered as hotspots for biogeochemical reactions (Vidon *et al.* 2010, Boano *et al.* 2014). The sensitivity of the CC measurement to the
physical properties of streambed sediments means that CC records distinctly different information from that obtained using temperature-based methods (e.g., fiber-optic distributed temperature sensing) that detect exchange locations based on the temperature contrast between groundwater and surface water (Briggs et al., 2012). The elevated $\sigma_{\text{sed}}^\prime$ responses in groundwater discharge zones in Mashpee River indicate increased specific surface area by Fe(III) oxide precipitates, which likely imply higher geochemical reaction rates due to the increased number of sites for both biotic and abiotic redox reactions.

In an additional application of CC measurements to a zone of known anoxic floodplain seepage along the larger alluvial East River (Colorado, USA), we found a similar correlation between $\sigma_{\text{sed}}^\prime$ and evidence of Fe(III) oxide precipitates to that observed in the Mashpee River. In East River, anoxic groundwater discharges were induced by floodplain beaver pond subsurface return flows, which produced visible rust-stained sediments indicating Fe(III) oxide precipitates (Briggs et al. 2019) (Figure C.3 in Appendix C). Distinctly higher $\sigma_{\text{sed}}^\prime$ (at 4 Hz) was acquired over these rust-stained sediments ($2.3 \pm 0.77 \mu \text{S cm}^{-1}$ from 22 different sites) relative to the more typically alluvial sediments along the main river channel ($0.26 \pm 0.37 \mu \text{S cm}^{-1}$ from 14 different sites) (Figure C.3 in Appendix C). In the same sites where we observed high $\sigma_{\text{sed}}^\prime$, Briggs et al., (2019) documented highly reduced floodplain groundwater upwelling with low dissolved oxygen, low redox potential and elevated concentrations of dissolved iron, manganese, aluminum and arsenic. The East River CC results support the transferability of CC measurements for detecting zones with high concentrations of Fe(III) oxides that may represent geochemical hotspots throughout different river corridor settings. Note that Fe(III) oxides can also be produced from other
processes such as acid mine drainage and hyporheic exchange. In these cases, mapping Fe(III) oxides may not provide information on the groundwater discharges, but still reveal important zones of high Fe(III) oxide concentrations that are critical to biogeochemical reactions and contaminant adsorption.

Our field CC methodology provides robust estimates of the electrical properties of streambed interface sediments, with immediate applications for advancing understanding of streambed dynamics. However, limitations remain in the proposed method. First, $\sigma''_{\text{sed}}$ is not solely controlled by one sediment property. The interpretation may be challenging when multiple properties vary spatially in the streambed. For example, the Mashpee River contains a relatively uniform sandy streambed with a relatively constant formation factor and porosity along the survey area so that the interpretation of $\sigma''_{\text{sed}}$ based on the variations in the Fe(III) oxide concentration is more reliable. In other cases, such as a coarse-bedded stream, the grain size distribution may influence the $\sigma''_{\text{sed}}$ response and would need to be taken into consideration. Secondly, CC measurements using a four-electrode method provide a relatively rapid evaluation of the streambed, but only measure the average responses from bulk sediment volumes at discrete locations. Considering the heterogeneity of the shallow streambed sediments, measurements using multielectrode arrays along a greater distance of the streambed would be needed to characterize more continuous horizontal and vertical variations of sediment properties. This will involve geophysical inversion along with a careful study of the impacts of the water layer on the inversion result (McLachlan et al., 2020). Finally, we mainly focused on single frequency data interpretation in this study. Considering the full CC spectra may ultimately provide
information on additional sediment properties, including particle/pore size distribution and possibly permeability.

5.6 Conclusions

Streambed interfaces are known to be highly reactive, impacting contaminant transport and nutrient availability, yet the sediment properties that impart a control on this reactivity, such as surface area, have been difficult or impossible to measure in situ. We have introduced a novel geophysical field application to characterize physical properties of shallow streambed sediments by CC measurements made at the water-streambed interface. An analytical model showed that measured imaginary conductivity has highly reduced sensitivity to the water layer, relative to real conductivity measured with the DC resistivity method. We use one case study to highlight the benefits of using imaginary conductivity for inferring variations in specific surface area, in this particular case, caused by precipitation of Fe(III) oxides associated with Fe-rich anoxic groundwater discharges. Laboratory analysis reveals a strong dependence of imaginary conductivity on sediment specific surface area. The spatial variation of field-acquired imaginary conductivity is consistent with that of sediment Fe(III) oxide concentration determining surface area; zones with elevated imaginary conductivity were located corresponding to enhanced Fe(III) oxide precipitation due to landfill leachate-impacted anoxic groundwater discharge. Consistent results were observed in an additional application in the East River (Colorado, USA), where relatively high imaginary conductivity was acquired in zones with high concentration of Fe(III) oxides induced by floodplain beaver pond subsurface return flow. This example demonstrates the transferability of CC measurements beyond one river.
corridor setting. The disagreements between laboratory and field measurements highlight the need for in situ measurements to fully represent the field conditions and meanwhile point out the importance of sensing scale when interpreting spatial variability. The proposed single array four-electrode streambed CC measurements serve as a reconnaissance tool for mapping spatial variations of sediment physical properties along a reach. Future work applying a 2D CC imaging survey using an array of electrodes might provide more continuous information on shallow streambed structure along tens of meters of the stream channel. The findings from this study are transferable to other surface water systems (e.g., lakes and marine environments) where physical variations in saturated sediments and clogging of pores with fines influences elemental cycling and groundwater-surface water exchange dynamics.

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improved this manuscript. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.
Chapter 6  Conclusions and Perspectives

This dissertation improved the understanding of spectral induced polarization (SIP) technique from different aspects. The findings and outcomes from each study potentially lead to new research topics in the SIP field. First, a novel correction method was developed to improve the laboratory SIP measurement accuracy at high frequencies (kHz range) (Chapter 3). Raw measurements made on electrical circuits and NaCl fluids with known phase responses showed phase errors up to hundreds of mrad at kHz frequencies, whereas the correction reduced the phase errors to less than 1 mrad. Applying the correction method to sand-clay and sand-pyrite mixtures removed the frequently observed dramatic increases of phase spectrum at kHz frequencies. This provided the opportunity to investigate the polarization at kHz frequencies that were seldomly explored due to the limitation of the measurement accuracy. On one hand, the Maxwell-Wagner polarization occurring at high frequencies can be better investigated and modeled. On the other hand, electrochemical polarization (the main focus of SIP research) at high frequencies can be better characterized. This will provide new insights into the electrical and physicochemical properties of small particles (e.g., clays and nanoparticles) that are important to various environmental processes. Moreover, SIP data at kHz bridge the lower frequency SIP spectrum and very high frequency (at MHz and GHz range) impedance spectroscopy data. This makes it possible to acquire wideband complex conductivity spectra spanning mHz to GHz, which potentially provides more information on the electrical behaviors for materials with broad relaxation.
Chapter 4 investigated the negative induced polarization (IP) phenomenon (i.e., positive apparent phase) in the SIP measurements. The results demonstrated that the polarity of the apparent phase was determined by the intrinsic phase distribution of the subsurface and the sensitivity distribution of a four-electrode measurement layout controlled by the intrinsic resistivity distribution. The simplest example to obtain negative IP data was to place a small, polarizable object within the negative sensitivity zones in a non-polarizable subsurface with homogeneous resistivity. For a real subsurface, the complicated patterns of heterogeneous resistivity and phase distribution make it difficult to generalize about the behaviors of negative IP data. It is important to not simply discard the negative IP data prior to inversion and interpretation in future field-scale studies. However, negative IP data may also arise from measurement errors. Future studies are needed to propose a methodology and algorithm to differentiate between erroneous and error-free negative IP data.

Chapter 5 developed a novel methodology using SIP to characterize the shallow streambed sediment physical properties in river corridors. The numerical results highlighted that the inverted sediment imaginary conductivity is less impacted by uncertainty in the water layer depth and conductivity relative to the real conductivity and phase shift. The laboratory and field results demonstrated the sensitivity of imaginary conductivity to high surface area iron oxide nanoparticles precipitated at anoxic groundwater discharge zones. The findings from this study can be extended in future studies. First, SIP signals of naturally occurred iron oxide nanoparticles are found to be distinct from sand and clay minerals. More detailed mechanistic and laboratory studies are needed to investigate the petrophysics of iron oxide
and its interaction with sand and clay minerals (e.g., coating and clogging). Secondly, this study focuses on the use of a single four-electrode array to sense shallow sediment at discrete locations. Future studies would apply multielectrode arrays to continuously image the 2D spatial variations of streambed properties. Moreover, long-term monitoring of SIP images may reveal more insights into the metal cycles and temporal variations of biogeochemical hot spots in river corridors.

Beyond the main research topics in this dissertation, other challenges remain in SIP geophysical method. First, the current petrophysical models are mostly established based on macroscopic-scale methods (e.g., volume average, effective medium methods) or empirical fitting using laboratory datasets. These methods generally involve many assumptions and result in simplified relationships between the SIP signal and one or more macroscopic-scale properties (e.g., specific surface area), which show high prediction uncertainties. Due to the large heterogeneity of Earth materials, numerical simulation at the microscale (pore or molecular scale) considering the microscale interactions, behaviors, and distribution may improve our understanding of SIP mechanisms to a new level. Secondly, the majority of SIP research is based on laboratory studies. Field SIP application is still challenging due to the complicated subsurface and higher noise in data acquisition. Future studies need to improve field SIP application to transfer laboratory findings to real cases. Finally, as a common challenge for all geophysical applications, it is difficult to reliably delineate the subsurface using the SIP technique only. While direct sampling and analysis are often performed to assist the interpretation of geophysical data, more can be done to improve our understanding. Studies integrate results from multiple methods (e.g.,
geophysical, hydrological, and remote sensing methods) at different scales will improve the delineation of the dynamic and heterogeneous subsurface.
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Appendices

Appendix A. Evaluation of riverbed magnetic susceptibility for mapping biogeochemical hot spots in groundwater-impacted rivers

Abstract

Redox hot spots occurring as metal-rich anoxic groundwater discharges through wetland and river sediments commonly result in the formation of iron (Fe) oxide precipitates. These redox-sensitive precipitates influence the release of nutrients and metals to surface water and can act as ‘contaminant sponges’ by absorbing toxic compounds. We explore the feasibility of a non-invasive, high resolution magnetic susceptibility (MS) technique to efficiently map the spatial variations of magnetic Fe oxide precipitates in the shallow bed of three rivers impacted by anoxic groundwater discharge. Laboratory analysis on Mashpee River (MA, USA) sediments demonstrate the sensitivity of MS to sediment Fe concentrations. Field surveys in the Mashpee and Quashnet rivers (MA, USA) reveal several discrete high MS zones, which are were associated with likely anoxic groundwater discharge as evaluated by riverbed temperature, vertical head gradient, and groundwater chemistry measurements. In the East River (CO, USA), widespread cobbles/rocks exhibit high background MS from ferrimagnetic minerals, thereby obscuring the relatively small enhancement of MS from groundwater induced Fe oxide precipitates. Our study suggests that in settings with low geologic sources of magnetic minerals such as lowland rivers and wetlands, MS may serve as a complementary tool to temperature methods for efficiently

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1 This content is under review in *Hydrological Process*. 
mapping Fe oxide accumulation zones at anoxic groundwater discharges that may function as biogeochemical hot spots and water quality control points in gaining systems.

A.1 Introduction

Rust-colored staining of interface sediments is frequently observed in streams, shallow rivers, and wetlands due to the precipitation of iron oxides and/or iron hydroxides (referred to here as Fe oxides). These Fe oxides are the result of biotic/abiotic redox reactions occurring when anoxic riverbed water rich in Fe(II) ions discharges through shallow oxic sediments and into surface water (Gandy et al. 2007, Boano et al. 2014). Fe oxide precipitates can result from anoxic groundwater discharge induced by anthropogenic contamination (Nordstrom 2011, Bakyayita et al. 2019) or natural biogeochemical reactions fueled by organic carbon (Baker et al. 2000) that mobilize and precipitate metals at redox interfaces. In addition to groundwater discharge sources, Fe oxides can also be produced by hyporheic and/or parafluvial (lateral) exchanges (Boano et al. 2014, Briggs et al. 2019). Fine-grained Fe oxides have large specific surface area, providing additional sites for biogeochemical reactions and sorption sites for a variety of contaminants, e.g., arsenic (Nagorski & Moore 1999), uranium (Winde & Van Der Walt 2004), and organic pollutants (Barber 1994, Gao & Chorover 2012). Therefore, river sediments containing Fe oxides can serve as important local contaminant sinks, although they can also serve as contaminant source points when Fe oxides are washed downstream or reduced to the dissolved phase during redox-sensitive biogeochemical reactions (Nagorski & Moore 1999). Efficient characterization of the spatial variability in Fe oxides deposited in the riverbed could reveal hot spots of biogeochemical reactions and contaminant adsorption,
being associated with anoxic discharge zones that can function as surface water quality control points (Briggs & Hare 2018). In addition, knowledge of the distribution of Fe oxides in riverbeds is also important to understanding of the availability of nutrients (e.g., nitrogen and phosphorus) and the sorption of isotope tracers for studying groundwater-surface water interactions (e.g., Radium-226) (Krishnaswami et al. 1982, Boulton et al. 1998).

Conventional methods for determining Fe oxide concentrations in the riverbed rely on extracting sediment samples and performing analysis in the lab (e.g., Håkansson et al., 1989; House et al., 1995). These methods are typically time consuming, generating low spatial resolution data and cannot provide in situ information on the sediments. Various temperature methods, e.g., fiber-optic distributed temperature sensing (Briggs et al. 2012, Hare et al. 2015, Rosenberry et al. 2016), streambed temperature mapping (Briggs et al. 2020), and thermal infrared imaging (Hare et al. 2015) have been widely applied in rivers to help geolocate groundwater discharge zones that may be associated with Fe oxide precipitation. However, these techniques are generally based on the natural temperature contrast between groundwater and surface water and do not directly indicate biogeochemical hot spots. Wang et al., (2020) explored the application of the complex electrical conductivity method to characterize shallow riverbed sediment surface area, from which the distribution of high surface area Fe oxides may be inferred. As Fe oxides are magnetic materials, a non-invasive magnetic susceptibility (MS) method might allow for a more rapid and direct assessment of river sediment Fe oxide distributions, providing
information on biogeochemically reactive groundwater/surface water exchange, although
MS has not previously been utilized for river corridor investigation.

MS quantifies the degree of magnetization of a material by an applied magnetic field
(Dearing 1999). We primarily focus on the volume MS, which is a unitless quantity
followed by ‘SI’ to indicate the use of the International System of Units. For ferromagnetic
materials like pure iron, the magnetic moments are highly ordered and aligned in the same
direction, which results in very high MS (e.g., 2172 SI). MS has been extensively used to
map buried iron metals associated with archaeological features (Dalan 2008). In geological
materials, ferrimagnetic materials like magnetite and maghemite also exhibit elevated MS
(e.g., 2.8 SI). Consequently, spatial and temporal variations of MS are normally considered
to result from variations of ferrimagnetic minerals in geological materials, from which
insights into a wide range of processes have been inferred, e.g., paleoclimate change (Q.
Liu et al. 2012), pedogenic processes (Verosub & Roberts, 1995), environmental impacts
(Desenfant et al. 2004), and iron cycling in hydrocarbon contaminated sites (Atekwana et
al. 2014, Lund et al. 2017). Other common naturally occurring Fe oxides including
hematite, goethite, ferrihydrite and lepidocrocite are either antiferromagnetic or
paramagnetic materials, which have weak MS. Most of the reported MS values of these Fe
oxides range between 1~5×10^{-3} SI, being two to three orders of magnitude smaller than
the MS of ferrimagnetic minerals (Blundell et al. 2009, Abdel Aal et al. 2014). The last
magnetic category is diamagnetic materials, in which the magnetic moments are weakly
aligned in the opposite direction of an applied magnetic field and therefore exhibit
negligible negative MS (e.g., −0.009×10^{-3} SI for water and −0.024×10^{-3} SI for quartz).
We hypothesize that for a riverbed sediment matrix with low (geologic) background MS, redox gradient-induced Fe oxide precipitates at redox interfaces may enhance MS signals. If so, field MS sensors could serve as efficient tools for locating zones with high concentrations of Fe oxides, potentially indicating anoxic discharge points that serve as hot spots of biogeochemical reactions. To test this hypothesis, we select three rivers with known zones of Fe oxide precipitates primarily induced by anoxic groundwater discharge. We first investigate the MS responses of sampled riverbed sediments at the laboratory scale. We then perform field surveys to investigate in situ the spatial variations of riverbed MS. We compare the MS measurements with groundwater discharge as evaluated with temperature, vertical head gradient, riverbed water dissolved oxygen, and specific conductance measurements, from which we discuss the hydrological process implications and benefits/limitations of new riverbed MS method.

A.2 Materials and Methods

The principle of riverbed MS measurements is illustrated in Figure A.1a. A planar MS probe is placed on the water-riverbed interface, which induces a magnetic field in the shallow sediments and records the resulting volume MS. Fe oxides precipitate and accumulate at redox interfaces where reducing aqueous Fe interacts with shallow oxidized environments (Figure A.1a). Over time, Fe oxide particles and coatings can mobilize and impact a larger volume of sediments up to the surface sediments (Runkel et al. 1999). Therefore, zones with relatively high concentrations of shallow Fe oxides may be revealed by high MS anomalies.
A.2.1 Study sites

The three studied rivers include the coastal Mashpee River (MA, USA), the nearby Quashnet River (MA, USA), and the montane East River (CO, USA) (Figure A.2). The Mashpee and Quashnet rivers are located in the same groundwater flow system (Sagamore flow lens) within the western Cape Cod aquifer (Walter et al. 2019). They are similar coastal streams, typically fed by a combination of upstream ponds and groundwater. The riverbeds of these two rivers are mainly composed of permeable glacial sediments dominated by sand/gravel grain sizes. In the Mashpee River, previous studies showed high nitrogen loading along the river corridor, in part resulting from upgradient landfill-sourced leachate that results in anoxic groundwater discharges to the river (Colman et al. 2004, Massachusetts. Bureau of Resource Protection 2006). In the lower Quashnet River, anoxic groundwater discharges are also widespread but generally attributed to more natural biogeochemical processes as groundwater flows through thick organic peat deposits in the streambed prior to discharge (Briggs, Harvey, et al. 2018). Briggs et al., (2020) also reported the occurrence of per- and poly-fluoroalkyl chemicals in more regional
groundwater discharge flow paths that also tended to be suboxic to anoxic. Therefore, Fe oxide precipitates are expected in both river sediments given the pronounced interactions between anoxic groundwater and oxic surface water. In contrast, the East River is a mountain alluvial river located in the Upper Colorado River Basin on the western slope (Hubbard et al. 2018). The riverbed in the region of study is dominated by large cobbles and shale bedrock outcrops at meander bend cutbanks. There are also broad floodplain areas that are well-connected to the channel via numerous beaver-induced water diversions. Briggs et al., (2019) characterized the focused anoxic groundwater discharge (induced by parafluvial subsurface return flows) downgradient of floodplain beaver ponds, which created reducing conditions, mobilizing metals from the floodplain sediments to the river.

Figure A.2 The locations of the studied rivers. Investigated river reaches are highlighted in red; white arrows represent the river flow directions.

A.2.2 Laboratory analysis of sediments
Riverbed interface sediments were sampled using a plastic scoop shovel and then dried and sieved for laboratory analysis. The solid Fe concentration of sampled sediments was determined by the ferrozine method (Stookey 1970), which measures the absorbance of the Fe(II) complex of ferrozine at 562 nm. Approximately 1 g of dried sediments was digested by 2 mL of 6 M HCl for one week to dissolve all the solid Fe oxides to aqueous Fe(II) and Fe(III). The acid digests were diluted accordingly for two analyses: (1) ferrozine reagent was added to determine Fe(II) concentration and (2) hydroxylamine hydrochloride was added to reduce all the Fe(III) to Fe(II) and then ferrozine reagent was added to determine the total Fe concentration. The Fe(III) concentration was then obtained by subtracting Fe(II) from the total Fe. Each sediment Fe concentration was measured in triplicate and reported as the average value with an associated standard deviation.

Laboratory scale MS measurements of sampled sediments were conducted using a Bartington MS2B sensor. Unconsolidated sediment samples were packed into a 10 ml cylindrical plastic bottle and then placed in the sensor cavity in which a low frequency magnetic field was induced to measure the mass MS (in m$^3$/kg). As the field MS probe measures the volume MS (dimensionless, SI), we converted the laboratory-measured mass MS to volume MS so that it can be compared to field measured MS directly. For each sample, the average volume MS from the three packings along with an associated standard deviation was recorded.

A.2.3 Field measurements
We applied two commercial MS instruments: (1) a KT-20-3F-32 probe (32 cm diameter, Terraplus, Inc.) for the Mashpee and Quashnet River studies, and (2) a MK250 probe (25 cm diameter, GF Instruments, s.r.o.) for the East River study. Both probes have a reported measurement sensitivity of 0.001×10⁻³ SI. A water-proof dry bag made of non-magnetic materials was used to protect the probe from the river water (Figure A.1b). Calibration tests confirmed that the dry bag had no impact on the measured signal magnitude or the data quality. The probe was calibrated in free space (open-air) before and after each riverbed sediment measurement to account for any signal drift in the sensor. Two different surveys were performed: (1) MS at discrete locations longitudinally along the river channel; (2) MS at discrete locations on a grid (5×5 m for Mashpee River and 1×1 m for East River) covering a small part of the river channel to investigate 2D MS variability in detail.

Supporting riverbed temperature and hydrologic data regarding the location and characteristics of groundwater discharges were collected to assist the interpretation of MS. In the Mashpee and Quashnet rivers, the riverbed temperature was recorded longitudinally along the river channel or on a grid corresponding to the MS measurements. A high precision digital thermometer (Traceable Thermometer, Control Company) was used with the needle probe pushed 10 cm into the sediments. The temperature \( T \), in °C) was recorded after the second decimal of the reading stabilized. The temperature difference between groundwater and surface water \( \Delta T \) was used as an indicator of groundwater discharges, a technique supported by numerous recent groundwater/surface water exchange studies in the region (e.g., Rosenberry et al., 2016; Briggs et al., 2020). In the representative locations characterized by high or low MS, 0.64 cm diameter stainless steel, push-point samplers
(MHE Products) were installed with the center of the 5-cm screen 20 cm below the sediment interface in order to extract sediment pore water samples and determine the hydraulic gradient relative to the stream water surface. A peristaltic pump was used to draw and collect the pore water via a soft transparent tube connected to the sampler. After removing the pump, the water level in the tube was recorded. Tube water levels higher than the river surface water were indicative of upwelling. In this case, a positive vertical head gradient (VHG) was determined from the difference between the water level inside the sampler tube and the river water surface divided by the depth of the screen (i.e., 20 cm). A SmarTroll MP handheld sensor (In-Situ Inc., United States) was used to record the surface water and the pore water/groundwater parameters including dissolved oxygen, specific conductance, and pH. In general, acquisition of MS and temperature data was fast (approximately 1 minute per measurement location), whereas push-point sampler measurements took much longer (0.5 to 1 h per location). For the East River, we used temperature and groundwater data collected along the study reach at the same time as this study and published in Briggs et al., (2019) to briefly discuss the shallow floodplain groundwater conditions. All the field surveys were conducted during summertime (July-August), when groundwater discharges are typically associated with relatively cold temperatures.

A.3 Results

Laboratory results are presented to demonstrate the influence of Fe oxides on the MS responses. Field results from three rivers are presented to show the spatial variations of MS and their potential association with anoxic groundwater discharges.
A.3.1 Laboratory analysis of sediment MS and Fe concentrations

Figure A.3 shows the relationship between MS and Fe concentrations of sediments sampled from different locations in Mashpee River. The concentration of total Fe, Fe(III) and Fe(II) ranges between 0.13–2.08%, 0.12–2.02% and 0.01–0.06%, respectively. Fe(III) dominates the Fe concentration and accounts for 90% to 97% of the total Fe. The laboratory measured MS ranges between $0.02 - 0.32 \times 10^{-3}$ SI and shows strong positive correlations with the Fe(III) and Fe(II) concentration ($R^2=0.87$ and 0.63, respectively). The laboratory analysis of one East River sediment sample shows a relatively high MS of $4.7 \times 10^{-3}$ SI corresponding to 2.6% total Fe, 2.3% Fe(III) and 0.3% Fe(II) (not shown in Figure A.3).

Figure A.3 Correlation between laboratory-measured MS and sediment Fe concentrations by weight. Panel a) shows Fe(III) and panel b) shows Fe(II). Analyzed sediments were sampled from Mashpee River and sieved to exclude grains larger than 2 mm.

Figure A.4 shows the Fe concentrations and MS responses from sieved sediments with different ranges of grain size. For the Mashpee and Quashnet river samples, Fe(III) and Fe(II) show similar trends with increasing grain size, with highest concentrations for the finest grains (<0.125 mm), decreasing to a low level in samples where grains range between 0.125 and 0.25 mm, remaining similarly low with increasing grain size (Figure A.4a and
A.4b). MS generally shows high responses for the finer grains and then decreases with increasing grain size. MS is lowest for the 0.5-1 mm grains, but then increases with increasing grain size to high values in the grains > 4 mm. In contrast, the East River sample is characterized by a weak dependence of Fe and MS on the sediment grain size (Figure A.4c).

![Graphs of Fe and MS analysis on sieved sediments containing high concentrations of Fe oxides from three rivers. (a) Mashpee River, (b) Quashnet River, and (c) East River. The x axis labels are grain size ranges in mm.](image)

Figure A.4 Fe and MS analysis on sieved sediments containing high concentrations of Fe oxides from three rivers. (a) Mashpee River, (b) Quashnet River, and (c) East River. The x axis labels are grain size ranges in mm.

### A.3.2 Field survey in Mashpee River
Field surveys were conducted across three selected sub-reach areas of the Mashpee River: MR1, MR2, and MR3 (Figure A.5). In sub-reach MR1, the riverbed temperature was generally close to the surface water temperature with $-4 \, ^\circ\text{C} < \Delta T < 0 \, ^\circ\text{C}$. Negligible VHGs was consistently observed from push-point sampler P1 installed in this area, indicating the lack of vertical groundwater discharge through the riverbed (Table A.1). In sub-reach MR2 and MR3, numerous cold spots with riverbed temperatures substantially lower than surface water temperatures were identified ($\Delta T$ up to $-10 \, ^\circ\text{C}$) (Figure A.5a). These cold spots are sparsely distributed along the river and sometimes only exist near the bank. Non-zero VHGs were determined by the push-point samplers P2-P7 installed in these sub-reaches, providing direct evidence of groundwater upwelling (Table A.1). The measured dissolved oxygen of pumped water from 20 cm sediment depth ranges between 0.59~9.94 ppm, where suboxic conditions indicate the contribution of anoxic groundwater.
Figure A.5 Field results from the Mashpee River. (a) Temperature difference between streambed and surface water (ΔT); MR1, MR2 and MR3 are three study areas corresponding to the locations in Figure A.1; triangle, circle and diamond symbols along MR2 are data measured near the eastern bank, middle of the river and western bank, respectively; MR3 contours represent an interpolation of data collected on a grid at the location indicated by the white block; arrows drawn parallel to the river indicate flow direction; P1 to P7 are push-point sampler installation locations, where surface water and groundwater properties were measured and shown in Table A.1; ‘x’ symbols in the contour indicate the push-point locations corresponding to P6 and P7 (b) MS measurements and laboratory measured sediment total Fe concentration; two dashed boxes highlight high MS zones, in which persistently elevated MS was observed along a substantial length of the study reach.
Table A.1 Surface water and groundwater properties. All non-zero VHG values indicate head increases with depth, i.e. upward vertical flow.

**Mashpee River**

<table>
<thead>
<tr>
<th>Sites †</th>
<th>Location ‡</th>
<th>$T$ (°C)</th>
<th>VHG (-)</th>
<th>DO (ppm)</th>
<th>SpC (μS/cm)</th>
<th>pH</th>
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<tr>
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<td>1.22</td>
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<td>6.39</td>
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</table>

**Quashnet River**

| P8      | S          | 19.61    | 8.86    | 114.4    | 6.42        |
|         | M          | 16.73    | 0.35    | 0.67     | 144         | 6.14 |
|         | E          | 15.23    | 0.10    | 0.99     | 179.8       | 6.59 |
|         | W          | 17.11    | 0.65    | 7.93     | 51.5        | 5.58 |
| P9      | S          | 19.33    | 7.75    | 108      | 6.42        |
|         | M          | 18.14    | 0       | 2.15     | 169.6       | 7.12 |
|         | E          | 18.92    | 0       | 1.9      | 83.7        | 6.93 |
|         | W          | 16.02    | 0.30    | 1.76     | 83.5        | 6.26 |

**East River §**

| P10     | S          | 19.28    | 9.03    | 261.4    | 8.58        |
|         | W          | 10.87    | NA      | 4.24     | 462.9       | 7.09 |

Column headings: $T$ (Temperature); VHG (Vertical head gradient); DO (Dissolved oxygen); SpC (specific conductance);
† Sites P1 to P7 are in the Mashpee River (indicated in Figure A.5); Sites P8 and P9 are in the Quashnet River (indicated in Figure A.7); Site P10 is in the East River (indicated in Figure A.8);
‡ ‘S’ represents surface water; ‘M’, ‘E’ and ‘W’ represent groundwater (or pore water when the VHG is 0) extracted from the riverbed near the middle, eastern bank and western bank, respectively; § Data from Briggs et al., (2019).

The MS signal in the Mashpee River mainly ranges from 0.1 to 0.7 ×10\(^{-3}\) SI, and shows different patterns in MR1, MR2 and MR3 (Figure A.5b). In MR1, the MS at each location exhibits a similar response with a relatively low average value of 0.28 ×10\(^{-3}\) SI. Elevated MS is observed in MR2, especially in the zones marked in the dashed square in Figure A.5b. The river segment along MR2 has a narrow channel, and most of the MS measurements near the banks are similar to those collected in the middle of the channel, although very low MS (~0.1 ×10\(^{-3}\) SI) near the bank was sometimes observed. In MR3, some localized zones with high MS up to 0.7 ×10\(^{-3}\) SI are observed. In general, variations of MS are consistent with the laboratory acquired sediment total Fe concentration, which generally increases from upstream to downstream in Mashpee River. The relationship between field MS and laboratory measured Fe concentration of interface sediments from corresponding locations in the Mashpee River is presented in Figure A.6. The correlations are analogous to that shown for the laboratory MS measurements. The slopes of the linear fits of the field MS-Fe(III) and field MS-Fe(II) trends are close to the slopes of the laboratory MS versus corresponding Fe concentration data. However, larger intercept values are observed for the linear fits to the field MS data.
Figure A.6 Correlation between field-measured MS and sediment Fe concentrations by weight. Panel a) shows Fe(III) and panel b) shows Fe(II). Sediments for Fe analysis are similar to those shown in Figure A.3 based on laboratory-measured MS.

A.3.3 Field survey in Quashnet River

Two sections of the nearby Quashnet River, sub-reaches QR1 and QR2, were investigated for this study (Figure A.7). In QR1, relatively low $\Delta T$ ranging between $-10 \sim -4$ °C is sporadically observed, indicating cold groundwater inputs (Figure A.7a). At the upstream end of QR1, both high and low oxygen groundwater is identified, with the VHG ranging between 0.1~0.65 and the DO ranging between 0.67~7.93 ppm (Figure A.4a and P8 in Table A.1). In contrast, QR2 is generally characterized as a reach of low groundwater input with most $\Delta T > -2$ °C. Consistently, two zero VHGs were measured in QR2 (P9 in Table A.1).

Strong MS around $1.0 \times 10^{-3}$ SI is observed in the middle of the channel at the upstream end of QR1. Similar to Mashpee River, some MS responses measured near bank are as low as $0.1 \times 10^{-3}$ SI. The MS measured in the middle of the channel decreases to $0.4 \times 10^{-3}$ SI towards downstream. In sub-reach QR2, most locations show consistently low MS responses around $0.2 \times 10^{-3}$ SI.
Figure A.7 Field results from the Quashnet River. (a) Temperature difference between streambed and surface water ($\Delta T$); QR1 and QR2 are two studied areas corresponding to the locations in Figure A.1; triangle, circle and diamond symbols are data measured near the eastern bank, middle of the river and western bank, respectively; arrows parallel to the river indicate river flow direction; P8 and P9 are push-point sampler installation locations, where surface water and groundwater properties were measured and shown in Table A.1. (b) MS measurements.

A.3.4 Field survey in East River

The results of the East River MS survey are presented in Figure A.8. A discrete, shallow floodplain groundwater upwelling zone with visible Fe seepage was observed downstream of a large beaver dam complex (described in Briggs et al., 2019), where riverbed MS measurements were performed on a grid (Figure A.5a). This groundwater was likely
influenced by reduced return flows from upgradient beaver ponds, with low dissolved oxygen and increased Fe concentration as high as 14,260.0 μg/L (Table A.1 and Briggs et al., 2019). The MS signals from 374 measurements shown in Figure A.5a range from 0.5 to $12.5 \times 10^{-3}$ SI, with an average value of $3.9 \times 10^{-3}$ SI. These responses are substantially higher than those observed in the Mashpee or Quashnet rivers, although the sediment total Fe is ~2.6%, and not remarkably higher than the MA rivers. Highest MS signals along this reach are not observed near the Fe groundwater discharge zones but are instead found near the opposite riverbank where no groundwater seepage was directly observed. The high MS signatures appear to be discontinuously distributed within the low MS background. The MS survey along the river reveals a relatively higher MS in the upstream 1 km relative to downstream locations (Figure A.8b). A temperature survey of this river section acquired using fiber-optic distributed temperature sensing at the same time with MS survey did not reveal any substantial cold anomalies along the river (Briggs et al 2019).

Figure A.8 Field MS survey in the East River. (a) Grid survey near a visible Fe seep; The groundwater and surface water properties at P10 are presented in Table A.1. (b) MS mapping along ~2.5 km river channel; arrows parallel to the river indicate river flow direction.
A.4 Discussion

The spatial variations of riverbed MS indicate the variations of magnetic minerals, which may result from sharp redox gradients generated at biogeochemical hot spots and/or background geological (sediment) sources. We identify two coastal rivers (Mashpee and Quashnet rivers) where the enhancement of riverbed MS is due to the precipitation of nanoparticle Fe oxides from the interactions between Fe-rich anoxic discharge and oxic surface water. This setting is contrasted to a western alluvial mountain cobbly riverbed (East River) where geologic MS signals appeared to swamp the biogeochemical signals. Below, we first discuss the controls of Fe oxides on the MS responses. We then discuss the potential associations between riverbed MS and the groundwater discharge zones in the studied rivers. Finally, we discuss general hydrological implications of the study and limitations of the MS technique.

A.4.1 Controls of Fe oxide on MS

Laboratory results of Mashpee River sediments demonstrate the sensitivity of MS to Fe variations (Figure A.3). The MS-Fe(III) relationship represents the contribution of MS from paramagnetic or antiferromagnetic Fe(III) oxides such as hematite, goethite, ferrihydrite and lepidocrocite. These Fe(III) oxides exist at relatively high concentrations and are responsible for the rust staining of riverbed sediment. In the MS-Fe(III) relationship, a small negative intercept is obtained which falls into a reasonable MS range between diamagnetic water \((-0.009 \times 10^{-3} \text{ SI})\) and quartz \((-0.015 \times 10^{-3} \text{ SI})\). The MS-Fe(III) relationship predicts an MS of \(~0.3 \times 10^{-3} \text{ SI}\) when Fe(III) is 2.0 % (Figure A.3a).
Assuming all the Fe(III) is from hematite ($\alpha$-Fe$_2$O$_3$) with a representative MS value of $4.5 \times 10^{-3}$ SI, and the hematite is uniformly distributed in a medium of 36% porosity (typical porosity for sandy sediments), the corresponding MS from hematite at Fe(III) concentration of 2% would be only $0.04 \times 10^{-3}$ SI which is significantly smaller than the measured signal (i.e., $\sim 0.3 \times 10^{-3}$ SI). Similar conclusions are obtained if we assume Fe(III) is from other common paramagnetic/antiferromagnetic Fe(III) oxides, as their MS are equally low. Therefore, the remaining portion of the MS signal must be from ferrimagnetic Fe oxides, most likely magnetite (Fe$_3$O$_4$) given its strong MS (e.g., $2,800 \times 10^{-3}$ SI). As a magnetite molecule (Fe$_3$O$_4$) contains one Fe(II) cation and two Fe(III) cations, an MS contribution from magnetite is consistent with the observed MS-Fe(II) correlation, which has a much larger slope than that of the MS-Fe(III) correlation (Figure A.3b). The measured Fe(II) may also result from other Fe(II) minerals with weaker MS (e.g., siderite, pyrite). This may explain the more negative intercept observed in the MS-Fe(II) relationship. While the concentrations of Fe(III) oxide dominate over magnetite, the MS contribution of magnetite is significant.

The laboratory analysis of MS and Fe on sieved sediments with various grain sizes highlights the contribution of nanoparticle Fe oxides in the Mashpee and Quashnet rivers (Figure A.4a and A.4b). These Fe oxides tend to aggregate with fine materials in pore spaces or coat onto relatively large grains. Therefore, consistently high Fe concentrations and MS are observed in the finest sediments. However, a relatively high MS is also observed in the coarse bed gravel sediments ($>2$ mm) even with low Fe concentrations. We attribute this high MS signal to trace amounts of magnetite embedded in large sediment
grains in this glacial outwash system, and are responsible for the background MS signal of coastal riverbed sediments. As the laboratory MS-Fe relationships (Figure A.3) were established using sieved superficial sediments with grain size less than 2 mm, this background MS from the bed gravels is not included, leading to the small intercept of the laboratory MS-Fe linear relationship. However, field MS-Fe linear relationships display larger intercepts representing this geological MS signal as the field probe senses larger volumes of sediments including large grains (Figure A.6). Nevertheless, the relative change of MS with groundwater discharge induced Fe oxides is large enough to be observed in Mashpee River sediments, as the background MS is relatively small and uniform (Figure A.6), indicating MS is an appropriate tool for mapping biogeochemical hot spots associated with anoxic discharge in similar settings.

In contrast, the MS of East River sediments is dominated by geological magnetite as evident from a much higher MS (~16 times of the maximum MS from Mashpee River sediments) and weak dependence of Fe and MS on grain size (Figure A.4c). This suggests that Fe is likely from the parent bedrock and therefore various grain size fractions have equally high Fe concentrations (Figure A.4c). In this case, variations of MS in samples from along the river reach primarily reflect geological variations and may fail to capture the magnetic signatures from groundwater discharge induced Fe oxides as discussed later in Section 4.2. This result indicates MS mapping may not capture biogeochemical hot spots in similar alluvial rivers, as the background magnetite-based signal dominates the bulk MS response observed with the field tool.
A.4.2 Field MS mapping

In Mashpee River, results from temperature and push-point sampler measurements demonstrate the high impacts of low oxygen, high specific conductance groundwater discharge in sub-reaches MR2 and MR3 (Figure A.5a and Table A.1). The leachate-impacted groundwater discharges in MR3 and downstream of MR2 result in elevated concentrations of Fe oxide precipitates, from which several discrete high MS zones are identified (Figure A.5b). The strong correlations between field-measured MS and Fe concentrations demonstrate the feasibility of using in situ MS measurements to efficiently map spatial variations of sediment Fe oxides (Figure A.6). As mentioned in Section 4.1, the large intercepts in the field MS-Fe relationship may represent the riverbed background MS signals, which are similar to the MS signals measured in MR1 characterized as no groundwater discharge and low Fe zones (Figure A.5). Overall, MS shows a strong dependence on both Fe(III) and Fe(II) in the riverbed sediments. We expect that formation of magnetite and Fe(III) oxides occurs simultaneously at the redox interface when anoxic groundwater mixes with oxic surface water. Although magnetite is not dominant as evident from the low sediment Fe(II) concentrations, its strong magnetic signature contributes to sensing relative variations in the Fe oxide concentration along a river corridor, which subsequently provides insights into the groundwater discharge. In the Quashnet River with its similar geological setting, similar associations between MS and groundwater discharges are identified. In general, high MS was detected at the upstream end of sub-reach QR1 with anoxic groundwater discharges, while low MS was detected in QR2 where no or limited groundwater discharge was identified (Figure A.7).
In the East River, the field MS survey revealed much higher responses than those measured in Mashpee and Quashnet rivers. We attribute the high MS to the geological background signals as extensive sources of magnetic minerals were identified in the upgradient mountain watershed (Langenheim Jr 1955, Gaskill et al. 1991). The spatially discrete high MS anomalies shown in Figure A.8a match the patterns of large cobble deposition along the riverbed interface. These cobbles originate from parent bedrock containing detrital ferrimagnetic magnetite associated with the Maroon formation (a Permian age sedimentary formation of primary Fe rich sandstone) (Langenheim Jr 1955). The high, geologically derived MS signal obscures the smaller MS increase due to Fe oxide precipitation from groundwater discharges. Therefore, the variations of MS may relate most strongly to riverbed geomorphology and depositional environment instead of groundwater discharge. Similarly, spatial variations of MS along the East River likely represent a change in geology of the source of shallow riverbed sediments (Figure A.8b). Alternatively, high MS signatures along the river might also indicate the formation of magnetite from certain biogeochemical reactions. As the river valley undergoes the snow and melt cycle during a year, the river sediments may experience anoxic environments that favor magnetite formation (Coates et al. 2001, Roh et al. 2003, Coker et al. 2006).

A.4.3 Applicability of riverbed MS surveys for mapping biogeochemical hot spots

We have demonstrated a novel potential application of MS to efficiently evaluate the magnetic properties of riverbed sediments. We mainly attribute the sediment MS responses to two sources including (1) the background MS from geological magnetic minerals and (2) the redox reaction induced nanoparticle Fe oxide precipitates associated with anoxic
discharges. In the Mashpee and Quashnet rivers with low background MS, anoxic groundwater discharge dominates the formation of Fe oxides. Therefore, combining MS surveys with hydrological surveys using conventional temperature and/or piezometer measurements may provide additional information on groundwater discharge patterns, thereby identifying potential biogeochemical hot spots. Enhanced Fe oxide precipitation in the riverbed represents strong redox gradients developed due to upward seepage/discharge having the combination of relatively high chemical flux and advective exchange, and can therefore be considered biogeochemical hotspots of relevance to instream processes.

Groundwater discharge zones with high MS may indicate anoxic groundwater flows with high concentrations of Fe and possibly other dissolved matter. For example, in the Mashpee River, high MS anomalies were located in zones with anoxic and high specific conductance groundwater discharge impacted by landfill leachates, the landfill thereby acting as a source of contamination to the river (Figure A.5 and Table A.1). In contrast, some groundwater discharge zones with low MS were found to have oxic and low specific conductance groundwater flows (e.g., push-point sampler P6-W in Table A.1 and Figure A.5).

While potential linkages between MS and groundwater conditions can be observed at specific sites, challenges remain for MS interpretation given the strong spatial and temporal variations of groundwater discharge and sediment Fe oxides. On one hand, temperature and MS data show high spatial variabilities even over small scales (Figures A.5 and A.7). This may indicate that groundwater inputs are dominated by locally focused or ‘preferential’ groundwater upwelling instead of more spatially diffuse discharge, as shown previously.
(Rosenberry et al. 2016, Briggs, Harvey, et al. 2018), and therefore biogeochemical conditions in the streambed are patchy. Fe oxide precipitates may also occur over a small region and may not be captured by discrete MS sensing. On the other hand, the location of Fe oxide precipitates may change over time with the transport of sediments. In the Mashpee and Quashnet rivers, sediment movement is likely to be small scale, with only the transport of Fe oxides in surficial sediments downstream. Therefore, zones containing transported Fe oxides accumulated in surficial sediments may not exhibit high MS. However, transported Fe oxides could continue to accumulate and impact a larger sediment volume in the long term. In this case, high MS zones will not indicate anoxic groundwater discharge locations but will still provide useful information on redistribution of Fe oxides by streambed processes. Such zones also serve as hot spots for biogeochemical reactions as the fine-grained Fe oxides serve as reaction sites. The high surface area of these Fe oxides also promotes sorption of contaminants entering streams. Therefore, geolocating these high Fe oxide zones using MS may help identify potential environmental quality control points for future studies. Note that Fe precipitates dominated by Fe(III) oxides do not show strong MS enhancement, and therefore may not be revealed in rivers with high background MS like East River.

While we mainly focus on the discussion of MS responses from Fe oxides induced by anoxic groundwater discharge, other riverbed processes involving formation and transformation of magnetic minerals may also be potentially revealed from MS surveys. For example, hyporheic exchange and acid mining drainage are also important sources for Fe oxide precipitates in riverbed sediments (Nagorski & Moore 1999, Akcil & Koldas 2006,
Such processes also generate biogeochemical hot spots and enhanced contaminant loads in river corridors that could be evaluated by MS measurements. Besides Fe oxides, nanoparticle Mn oxide precipitates (visually identifiable as black coatings on sediments) are widespread when groundwater or hyporheic flow containing high concentrations of aqueous Mn(II) mixes with surface water (Harvey & Fuller 1998). Although Mn oxides have generally lower MS than Fe oxides, they may generate detectable MS signals when they are the dominant magnetic minerals (Emerson & Schmidt 2018). In some river environments, including polluted or naturally saline rivers, sulfate reduction is a dominant biogeochemical process resulting in the formation of iron sulfides such as FeS₂ and FeS with weak MS. Consequently, MS measures the cumulative signature resulting from magnetic minerals accumulated in the riverbed. Therefore, prior information or a limited amount of direct sampling and analysis is required to reliably interpret MS data in terms of specific mineral forming processes occurring in the riverbed sediments. However, ferrimagnetic magnetite, having a much stronger MS than other minerals, is often likely to dominate the MS signal.

A.4.4 Limitations and future directions of MS technique

MS has been widely used to study the magnetic properties of soils and rocks, whereas it has not been applied to characterize riverbed sediments in situ. We explored the feasibility of using the MS technique to locate high Fe oxide zones that may be potentially linked to anoxic groundwater discharges. The MS technique has advantages including easy implementation (small instrument size, Figure A.2b) and fast data acquisition (5 ~ 10 seconds per reading). This makes MS a useful complementary tool to temperature-based
methods for efficiently surveying groundwater discharges in rivers. However, limitations remain concerning the methodology and data interpretation. These include: (1) Deployment of a commercially available MS sensor required a waterproof bag to protect the MS probe, limiting application to shallow water environments (river water depth < 80 cm); (2) The MS measurement depth is fixed and determined by the coil size in the probe. Adjusted MS measurement depths will provide more comprehensive information on the distribution of magnetic minerals with depth as the redox conditions vary with sediment depth. (3) Riverbed MS may exhibit high spatial variability even over small areas of the riverbed. More continuous surveys might capture details of the heterogeneous distribution of iron oxides reflecting complex hydrological and biogeochemical processes occurring in riverbed sediments; (4) Various processes and geological minerals can contribute to MS variations; additional supporting information from other complementary techniques will improve interpretation of streambed processes; applying MS alone may not accurately determine the distribution of anoxic groundwater discharge zones.

A.5 Conclusion
We applied a non-invasive, efficient magnetic susceptibility (MS) field reconnaissance method to investigate patterns in Fe oxide precipitates in shallow riverbed sediments that are often associate with biogeochemical hot spots. Laboratory experiments show that MS is strongly correlated with Fe(III) and Fe(II) concentrations, but is dominated by ferrimagnetic magnetite. Laboratory Fe and MS analyses on the sieved sediments reveal two primary MS sources including the redox reaction produced nanoparticle Fe oxide precipitates and the geologically formed background Fe oxide minerals. In the Mashpee
and Quashnet rivers with low MS from background Fe minerals, MS is effective in locating high Fe oxide concentration zones impacted by anoxic groundwater discharges embedded in complex groundwater gaining systems. Studies in the East River show much higher MS signals resulting primarily from variations in the parent geology of cobbles, which may provide information on the geological variations of shallow riverbed minerals, but MS will not be useful for mapping biogeochemical hot spots associated with floodplain seepages in that alluvial. The high MS locations identified in the Mashpee and Quashnet rivers indicate high concentration of Fe oxide precipitates, which could be potential environmental risk zones absorbing high concentration contaminants. Further studies at these locations might include quantification of contaminants absorbed on the sediment Fe oxide precipitates located with MS to better understand fate and transport processes along the reactive river corridor.

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manuscript.
Appendix B. Supporting information for Chapter 3

B1. Verification of the accuracy of Eq. (14)

To evaluate if the simplifications invoked in the derivation of Eq. (3.14) are valid, 4,374 synthetic circuits were established by combining different parameter options shown in Table B.1. Each parameter was assumed to be frequency independent for simplification. All the combinations fulfill the criteria applied in the derivation and cover the range of parameters obtained in the real samples in this study. Given a random input voltage, the true measured impedance magnitude and phase for each circuit at any frequency can be solved explicitly using Eqs (3.5) and (3.11). Meanwhile, the predicted measured magnitude and phase can be calculated using the simplified Eq. (3.14). Computations for each circuit were conducted at 14 equally spaced frequencies between 1 and 20 kHz. Figure B.1 shows that Eq. (3.14) accurately predicts the measured phase for all the synthetic circuits with most errors less than 5%. In addition, all the true measured magnitudes have less than 5% errors from the sample magnitudes (data not shown), being consistent with Eq. (3.14).

Table B.2 Parameters used for the synthetic circuits.

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<td></td>
<td>$\phi_{e,p} (\text{mrad})^*$</td>
<td>10, 50, 100</td>
</tr>
<tr>
<td>$-\phi_{e,n}$ (mrad)$^*$</td>
<td>$-\phi_{ep}$ ***</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Instrument</strong></td>
<td><strong>$C_{in}$ (pF)</strong></td>
<td><strong>8.9</strong></td>
</tr>
<tr>
<td></td>
<td><strong>$R_{ref}$ (Ω)</strong></td>
<td>**0.2 $</td>
</tr>
<tr>
<td></td>
<td>**$</td>
<td>Z_s</td>
</tr>
</tbody>
</table>

*$^*$ Parameters were not considered when predicting phase errors using Eq. (3.15).

** $^*$ We made $-\phi_{e,n}$ slightly higher than $-\phi_s$ due to the additional phase from contact impedance.

*** $^*$ We assumed both potential electrodes have the same phase response.

Figure B.1 Comparison between predicted phase error using simplified Eq. (3.14) and true phase error calculated using original Eqs (3.5) and (3.11). Black dots include all the data calculated from 4,373 synthetic circuits at 14 equally spaced frequencies from 100 Hz to 20 kHz.
Appendix C. Supporting information for Chapter 4

C1. Derivation of analytical solution

To derive the analytical solution of streambed complex conductivity measurement made at
the water-sediment interface, we first explain the general single overburden problem
described in Keller and Frischknecht (1966). Consider a current source C with current
intensity \( I \) in a medium (with thickness \( d \) and resistivity \( \rho_1 \)) located between two semi-
infinite media (with resistivity \( \rho_0 \) and \( \rho_2 \), respectively) (Figure C.1a). The distance between
C and the upper boundary is \( h \). A potential measuring point P is located horizontally from
C at a distance \( r \) where the potential \( (U_p) \) contains contributions from both the primary
current source C as well as its images resulting from the reflections in the same manner as
optical pathways (Figure C.1b). The potential from the primary source \( (U_0) \) is,

\[
U_0 = \frac{\rho_1 I}{4\pi r}.
\]  

(C.1)

To calculate the potential from image current sources, four different types of reflection
pathways need to be considered: type 1 first reflects from the upper boundary and creates
an image in medium 0; type 2 first reflects from the upper boundary and creates an image
in medium 2; type 3 first reflects from the lower boundary and creates an image in medium
0 and type 4 first reflects from the lower boundary and creates an image in medium 2
(Figure C.1b).
Figure C.1 Illustration of current reflection between two boundaries. (a) Problem description; (b) Four different types of current reflection; (c) Type 1 reflection with two reflections from the upper boundary; (d) Type 1 reflection with three reflections from the upper boundary.

Take type 1 reflection as an example. As it reflects from the upper boundary once, the resultant image source $C^{(1)}_1$ (where subscript 1 represents type 1 reflection and superscript (1) represents one reflection from the boundary it first reaches, i.e. upper boundary for type 1 reflection) has a current intensity $I_{k1,0}$. $k_{1,0}$ is the reflection coefficient for the boundary between medium 1 and 0 when viewed from medium 1, and has the expression,

$$k_{1,0} = \frac{\rho_0 - \rho_1}{\rho_0 + \rho_1}. \quad (C.2)$$

The potential from this image current source $C^{(1)}_1$ is obtained as,
The type 1 reflection can also reflect twice from the upper boundary and once from the lower boundary to reach point P as shown in Figure C.1c. The resultant image source $C_1^{(2)}$ has a current intensity $I_k^{2} k_{1.2}$, where $k_{1.2}$ is the reflection coefficient for the boundary between medium 1 and 2 when viewed from medium 1. The potential produced by $C_1^{(2)}$ at P is,

$$U_1^{(2)} = \frac{\rho_1 I k_{1,0}^2 k_{1,2}}{4\pi \sqrt{r^2 + (2d + 2h)^2}}. \quad (C.4)$$

Similarly, $C_1^{(3)}$ produced by three reflections from the upper boundary (Figure C.1d) gives P a potential,

$$U_1^{(3)} = \frac{\rho_1 I k_{1,0}^3 k_{1,2}^2}{4\pi \sqrt{r^2 + (4d + 2h)^2}}. \quad (C.5)$$

There are unlimited pathways for type 1 reflection and their collective contribution to the potential at point P will be,

$$U_1 = \sum_{n=1}^{\infty} \frac{\rho_1 I k_{1,0}^n k_{1,2}^{n-1}}{4\pi \sqrt{r^2 + [2(n-1)d + 2h]^2}}. \quad (C.6)$$

Applying the same derivation approach, we get the potential contributed from type 2 ($U_2$), type 3 ($U_3$) and type 4 ($U_4$) reflections,

$$U_2 = \sum_{n=1}^{\infty} \frac{\rho_1 I k_{1,0}^n k_{1,2}^n}{4\pi \sqrt{r^2 + (2nd)^2}}. \quad (C.7a)$$
\[ U_3 = \sum_{n=1}^{\infty} \frac{\rho_1 l k_{1,0}^n k_{1,2}^n}{4\pi \sqrt{r^2 + (2nd)^2}}, \]  
(C.7b)

\[ U_4 = \sum_{n=1}^{\infty} \frac{\rho_1 l k_{1,0}^{n-1} k_{1,2}^n}{4\pi \sqrt{r^2 + [2(n - 1)d + 2(d - h)]^2}}. \]  
(C.7c)

\[ U_p \] is obtained by summing up the potential contributions from the primary source \((U_0)\) and image sources \((U_1, U_2, U_3\) and \(U_4)\). For the streambed complex conductivity measurement described in Figure 5.1b, we have \(d = h\) and \(k_{1,0} = 1\) (medium 0 is air and has \(\rho_0 = +\infty\)). \(U_p\) is then simplified as,

\[ U_p = \frac{\rho_1 l}{4\pi r} + \sum_{n=1}^{\infty} \frac{\rho_1 l k_{1,2}^n}{4\pi \sqrt{r^2 + (2nd)^2}} + \sum_{n=1}^{\infty} \frac{\rho_1 l k_{1,2}^n}{4\pi \sqrt{r^2 + (2nd)^2}} + \sum_{n=1}^{\infty} \frac{\rho_1 l k_{1,2}^n}{4\pi \sqrt{r^2 + [2(n - 1)d + 2d - h)]^2}}. \]  
(C.8)

Combine the series in Eq. (C.8) and rewrite Eq. (C.8) as,

\[ U_p = \frac{\rho_1 l}{4\pi r} \left[ 1 + k_{1,2} + \sum_{n=1}^{\infty} \frac{k_{1,2}^{n-1} (k_{1,2} + 1)^2}{1 + (2nd/r)^2} \right]. \]  
(C.9)

Substituting all the resistivity terms by complex conductivity terms gives Eq. (5.13) in the main text.
Figure C.2 Synthetic modeling results of streambed CC measurements using different electrode arrays. The models include a homogeneous sediment layer with $\sigma'_{\text{sed}} = 25 \ \mu \text{S cm}^{-1}$ and $\sigma''_{\text{sed}} = 0.5 \ \mu \text{S cm}^{-1}$ ($\phi_{\text{sed}} = 20 \ \text{mrad}$) beneath a water layer with varying $d$ and $\sigma_w$. (a) Array description; (b) Wenner array; (c) Schlumberger array; (d) Dipole-dipole array.
Figure C.3 Field study in the East River (Colorado, USA). (a). Comparison of in-situ measured $\sigma_{\text{sed}}$ between a side channel and the adjacent main channel; (b). The photo of the surveyed side channel showing visible Fe(III) oxide precipitation induced by anoxic groundwater discharge.