

Tracing reaction dynamics with Spectral Induced Polarization

Dissertation

der Mathematisch-Naturwissenschaftlichen Fakultät
der Eberhard Karls Universität Tübingen
zur Erlangung des Grades eines
Doktors der Naturwissenschaften
(Dr. rer. nat.)

vorgelegt von
M.Sc. Cora Strobel
aus Tübingen

Tübingen
2024

Gedruckt mit Genehmigung der Mathematisch-Naturwissenschaftlichen Fakultät der
Eberhard Karls Universität Tübingen.

Tag der mündlichen Qualifikation:

12.11.2024

Dekan:

Prof. Dr. Thilo Stehle

1. Berichterstatter/-in:

Prof. Dr. Adrian Mellage

2. Berichterstatter/-in:

Prof. Dr. Reinhard Drews

Contents

Abstract	III
Zusammenfassung	VI
Acknowledgements	IX
List of publications	XI
Abbreviations	XII
1. Introduction	1
2. State of the art: SIP as a monitoring tool?	4
3. Objectives	17
4. Results and discussion	19
4.1. Background polarization of organic matter - Why solid organic matter matters in induced polarization measurements	19
4.2. Monitoring of abiotic cation exchange - towards online monitoring with SIP	23
4.3. Distinguishing between biotic and abiotic reactions	29
5. Conclusions and outlook	35
6. References	39
A. Appendix	53
A.1. Publication 1	53
A.2. Publication 2	75
A.3. Publication 3	86
A.3.1. Publication 3: supporting information	121

Abstract

Given its limited accessibility, the subsurface is often a "black box" regarding its potential for (bio)geochemical reactions and capability to degrade contaminants. Point information at monitoring wells only provides a "blurred glimpse" into this black box. They lack the spatial resolution necessary to identify and quantify the reactive potential. In particular, information on the solid phase, namely concentrations of surface associated compounds and the composition and abundance of microbial communities is challenging and often impossible to be acquired. Hence, methods that address the characterization gap between traditional sampling methods are required. Spectral induced polarization (SIP) can provide valuable information about processes that alter the surface chemistry/composition of the solid phase in a non-invasive manner and is therefore well poised to complement geochemical analytics. Solid particles suspended in water carry a surface charge that induces the orientation and alignment of counter ions in the water phase surrounding the solid's surface, known as the electrical double layer (EDL). SIP polarizes the EDL by applying an alternating-current field of defined frequency, and measures the corresponding alternating voltage response. As such, SIP is potentially sensitive towards a series of different reactions and complements pore water samples as it provides information on the solid phase without sampling it.

In my thesis, I explore the potential of SIP as a method to monitor reactions under increasingly complex conditions. I analyze the polarization response of natural organic matter and microbial activity, which has not been well understood before, in several experiments. In the first part of this dissertation I show how important the polarization of organic matter is as a background signal in sediment mixtures. I demonstrate that the knowledge on electrochemical polarization of mineral surfaces can be transferred to organic matter by using the cation exchange capacity as a predictor for polarization strength. To this end, I investigate the SIP signal of artificial mixtures of peat and sand made of calcite under controlled conditions and in fresh, undisturbed field cores. I show that even low organic matter contents can

cause a significant polarization signal, potentially interfering with petrophysical relationships.

In nature, multiple and often coupled polarization processes co-occur, highlighting the need to distinguish different signal contributions when applying SIP in the environment. I present a framework on how and under which conditions SIP is a suitable online monitoring method that can guide traditional sampling events or predict the duration and spatial extend of a reaction. To this end, I use cation exchange reactions on organic matter, monitored in flow-through columns as model reactions in the second part of this dissertation. I investigate how the signal stemming from the change in the EDL can be separated from a change in the pore water salinity. I apply a reactive transport modeling based approach, in which the SIP signal serves as a proxy for the sorbed concentration of the injected cation. The change induced by electrical conductivity is removed assuming a proportionality with the concentration of the non-reactive solute. With this approach, SIP data can be incorporated quantitatively into reactive transport models, providing highly-resolved information on the solid phase concentrations. Additionally, I show how SIP data can be visualized to serve as a monitoring tool that operates independently of geochemical samples.

In the third part I show that SIP is sensitive enough to monitor changes in microbial activity and abundance under quasi-natural conditions in column experiment. Therefore, I stimulate a natural microbial community in flow-through columns within its natural sediment through the amendment of nitrate into the inflowing solution. The results show that, even in the presence of parallel polarization processes under field-relevant geochemical conditions, SIP is sufficiently sensitive to monitor microbially-mediated reactions. I propose a decomposition of the SIP signal to separate the effect of microbial activity from abiotic cation exchange and show how this method can clearly identify zones and times of high microbial activity without the need for an additional geochemically-informed reactive transport model.

This thesis highlights workflows and conditions that need to be met so that our view into the “black box” of the subsurface is sharpened. It lays out how informa-

Contents

tion obtained from SIP measurements can be used to fine tune sampling campaigns, locate microbially active zones, and constrain solid phase concentrations in models.

Zusammenfassung

Aufgrund seiner begrenzten Zugänglichkeit ist der Untergrund für Umweltwissenschaftler oft eine „Black Box“. Es ist oft unklar welche (bio)geochemische Reaktionen und ob der Abbau von Schadstoffen vor Ort stattfinden (können). Informationen aus Grundwassermessstellen bieten nur begrenzte Einblicke und haben nicht die räumliche Auflösung, die zur Identifizierung und Quantifizierung des reaktiven Potenzials notwendig ist. Besonders Informationen über Stoffe, die auf dem Sediment sorbiert sind Zusammensetzung mikrobieller Gemeinschaften, sind schwer zu bekommen. Daher brauchen wir Methoden, die diese Informationslücken schließen können.

Die spektrale induzierte Polarisation (SIP) kann auf nicht-invasive Weise wertvolle Informationen über Prozesse liefern, die die Oberflächenchemie &-zusammensetzung der festen Phase verändern. Dadurch ist sie gut geeignet, die „klassische“ geochemische Analytik zu ergänzen. In Wasser suspendierte Partikel haben eine Oberflächenladung, die die Ausrichtung von Gegenionen in der Wasserphase um die Partikel, der sogenannten elektrischen Doppelschicht (EDS), beeinflusst. SIP polarisiert die EDS durch Anlegen eines Wechselstromfeldes mit definierter Frequenz. Dadurch ist SIP empfindlich für verschiedene Reaktionen und ergänzt Grundwasserproben, da es Informationen über die feste Phase liefert, ohne diese beproben zu müssen.

In meiner Dissertation untersuche ich das Potenzial von SIP als Methode zur Überwachung von Reaktionen unter immer komplexeren Bedingungen. In mehreren Experimenten analysiere ich die SIP-Signale organischer Materie und mikrobieller Aktivität, die noch nicht vollständig verstanden sind. Im ersten Teil dieser Dissertation zeige ich, wie wichtig die Polarisation organischer Materie als Hintergrundsignal in Sedimentmischungen ist. Ich zeige, dass das Wissen über die elektrochemische Polarisation von mineralischen Oberflächen auf organisches Material übertragen werden kann, indem die Kationenaustauschkapazität als Maß für die Polarisationsstärke verwendet wird. Dafür untersuche ich das SIP-Signal von Mischungen aus Torf und Calcit-Sand unter kontrollierten Bedingungen und in frischen Feldkernen.

Ich zeige, dass selbst geringe Mengen an organischer Substanz ein signifikantes Polarisationsignal verursachen können, das unter bestimmten Bedingungen petrophysikalische Modelle stören kann.

In der Natur treten oft mehrere Polarisationsprozesse gleichzeitig auf, was die Notwendigkeit zeigt, bei der Anwendung von SIP in der Umwelt zwischen verschiedenen Signalbeiträgen unterscheiden zu können. Ich zeige, wie und unter welchen Bedingungen SIP eine geeignete Methode ist, um traditionelle Probenahmeereignisse zu planen oder die Dauer und räumliche Ausdehnung einer Reaktion vorherzusagen. Dafür verwende ich im zweiten Teil Kationenaustauschreaktionen an organischem Material als Modellreaktionen, die in Säulenexperimenten beobachtet werden. Ich untersuche, wie das von der Änderung der EDS herrührende Signal von einer Änderung der elektrischen Leitfähigkeit im Porenwasser getrennt werden kann. Um den Kationenaustausch zu beschreiben, wende ich ein Transport-Modell an, bei dem das SIP-Signal als Maß für die sorbierte Konzentration des injizierten Kations dient. Mit diesem Ansatz können SIP-Daten in reaktive Transportmodelle integriert werden und liefern hochaufgelöste Informationen über die Festphasenkonzentrationen. Außerdem zeige ich, wie SIP-Daten visualisiert werden können, um als Beobachtungsmethode zu dienen, die unabhängig von geochemischen Proben funktioniert.

Im dritten Teil zeige ich, dass SIP empfindlich genug ist, um Veränderungen der mikrobiellen Aktivität und Menge unter quasi-natürlichen Bedingungen in einem Säulenexperiment zu überwachen. Dazu stimulierte ich eine natürliche mikrobielle Gemeinschaft in Durchflusssäulen innerhalb ihres natürlichen Sediments durch die Zugabe von Nitrat. Die Ergebnisse zeigen, dass SIP selbst bei Vorhandensein paralleler Polarisationsprozesse unter feldrelevanten geochemischen Bedingungen ausreichend empfindlich ist, um mikrobielle Aktivität zu beobachten. Ich schlage eine Zerlegung des SIP-Signals vor, um den Effekt der mikrobiellen Aktivität vom abiotischen Kationenaustausch zu trennen, und zeige, wie diese Methode Zonen und Zeiten hoher mikrobieller Aktivität eindeutig identifizieren kann, ohne dass zusätzliche Daten oder ein zusätzliches Transportmodell erforderlich sind. Diese Arbeit zeigt Arbeitsabläufe

und Bedingungen auf, die erfüllt sein müssen, damit unser Blick in die „Black Box“ des Untergrunds mittels SIP geschärft werden kann. Ich diskutiere und zeige, wie die aus SIP-Messungen gewonnenen Informationen zur Planung von Probenahmekampagnen, zur Lokalisierung mikrobiell aktiver Zonen und zur Bestimmung der Festphasenkonzentrationen verwendet werden können.

Acknowledgements

I would like to extend my deepest gratitude to the many individuals who have supported me throughout the journey of my PhD.

- First and foremost, I am immensely grateful to my supervisor, Adrian, for providing the perfect mix of freedom, flexibility, and guidance. Your excitement about the results is contagious and your great feedback culture have been invaluable to me.
- Thank you Olaf for your supervision, for being the most critical reviewer of my work and still letting me follow my own path and for having me stay as part of your group in Tübingen.
- Sander, thank you for joining my thesis committee and providing your expertise and experience working with IP data (acquisition)
- Carsten, your numerous practical tips, quick fixes, help with the installation of the field site, and assistance with field work were indispensable.
- I would also like to thank my co-authors: Sergey and Anna S. for providing me valuable insights into your research expertise and improving our manuscripts with your input. Manuel and Emma for your conscientious and independent lab work, which allowed me to conduct all the experiments during my pregnancy and gave me all the data to analyze upon returning from my parental leave.
- I am grateful to Bernice, Franzi, and Björn for analyzing hundreds of samples, and to all the lab technicians and Daniel for maintaining a well-organized environment that greatly accelerated our lab success. A special thanks to Marc for his field work and for building our field electrodes even without a running workshop.
- To my office mates, Marie-Madeleine and Johan, thank you for the fantastic and open conversations about science and beyond, for bringing color and atmosphere into the office, and for tolerating Toffie. Joni, I won't forget our countless

lunchtime conversations and thank you for motivating and pushing me when I doubted myself. Anna R., thank you for our lunch talks that extended beyond academia, for keeping in touch during my leave, and for your emotional support as I worked to finish up. To the entire Level 4 crew, thank you for the friendly atmosphere and between-door conversations.

- I would like to express my gratitude to the Hydrogeology group in Tübingen and Kassel including former members, especially Jonas, Stefan, and Simon, for the open and welcoming working environment, the group lunches and to Janek for restarting the cake tradition. To Ali, Vitor, Lysander and Dinithi: thanks for having me feel part of your team despite the distance and for the fantastic barbecue and good vibes!
- To my family and friends, your support throughout my studies and the journey of my PhD has been invaluable. Each of you has helped me in many different ways, and I owe you so much Helmut, Brigitte, Urs, Hannes, Johanna, Jasmin, Eva, Elena, Caro, Rami & Ina. Without the constant support of my parents, my university education would not have been possible.
- Jonah, your smile and laughter have motivated me as nothing else could. Thank you!
- Finally, to Noam, finishing this PhD would have been impossible without you by my side. Thank you for your patience when I missed the bus or had to go to the lab or field at odd hours, for your flexibility in our vacation plans, for making the best cappuccinos, and most importantly, for being the best father to our son.

List of publications

Publication 1 Strobel, C., Abramov, S., Huisman, J. A., Cirpka, O. A., & Mollage, A. (2023). Spectral Induced Polarization (SIP) of Denitrification - Driven Microbial Activity in Column Experiments Packed With Calcareous Aquifer Sediments. *Journal of Geophysical Research: Biogeosciences*, 128(1)
<https://doi.org/10.1029/2022JG007190>

Author contributions: The conceptualization of this work was done by CS and AM with feedback by JAH and OAC. The experiments, data curation, analysis and visualization were conducted by CS, experimental methods development was done by CS, SA and AM. SA was in charge of the qPCR and microbial microscopy. The reactive transport model was developed by CS and AM based on a code by OAC. CS wrote the original manuscript draft and conducted the submission and review process and all authors contributed to the review and editing of the original draft and during the review process. AM, JAH and OAC supervised the entire project, AM and OAC provided the resources to conduct this research.

Publication 2 Strobel, C., Doerrich, M., Stieff, E. -H., Huisman, J. A., Cirpka, O. A., & Mollage, A. (2023). Organic Matter Matters — The Imaginary Conductivity of Sediments Rich in Solid Organic Carbon. *Geophysical Research Letters*, 50(23), e2023GL104630 <https://doi.org/10.1029/2023GL104630>

Author contributions: The conceptualization of this work was done by CS, with feedback by AM, JAH, OAC. The experiments were conducted by ES and MD with supervision by CS. CS performed the SIP measurements. CS performed the data curation, formal analysis, visualization and wrote the original draft. AM, JAH and OAC supervised the entire project and reviewed the manuscript draft. AM and OAC provided the resources to conduct this research. The submission and review process was conducted by AM with input from CS, JAH and OAC.

Publication 3 Strobel, C., Störiko, A., Cirpka, O.A., & Melling, A. (2024). Are we there yet? A critical experimental assessment of the application of induced polarization for monitoring geochemical processes, *accepted by: Water Resources Research*

Author contributions: The conceptualization of this work was done by CS, with feedback by AM and OAC. The experiments were planned and conducted by CS. CS performed the data curation, formal analysis, visualization and wrote the original draft. AS wrote the reactive transport model with input by CS and performed the Bayesian parameter estimation. AS, OAC and AM reviewed the manuscript draft and OAC and AM provided the resources to conduct this research and supervised the project.

Abbreviations

CEC	cation exchange capacity	10
DC	direct current	7
EC	electrical conductivity	24
EDL	electrical double layer	4
OM	organic matter	4
RTM	reactive transport model	3
SIP	spectral induced polarization	4
TOC	total organic carbon	20

1. Introduction

Groundwater is our largest available freshwater resource. It is of utmost importance as it provides clean water for irrigation (>70%), households and industry [Smith et al. 2016]. However, human activity and geologic processes cause the contamination of groundwater with organic and inorganic toxic substances such as hydrocarbons, chlorinated solvents and other organic substances [Suarez and Rifai 1999; Lapworth et al. 2012], nitrate [Rivett et al. 2008a; Wick et al. 2012] or heavy-metals [Podgorski and Berg 2020]. Depending on the source, such groundwater contaminations can occur widespread over an entire aquifer, or as spatially contained plumes. It is a major task of groundwater management to contain them and prevent them from polluting wells used for drinking water production or irrigation [Smith et al. 2016].

Once introduced into the aquifer, contaminants can be transported by groundwater flow, sorb onto the sediments' surface, form a non-aqueous liquid phase or undergo (microbially-mediated) transformation reactions or precipitation/dissolution reactions [Fetter 2008]. Generally speaking, a reaction requires that all reactants meet on microscopic scales in the subsurface and have a sufficient contact time to react. That is, the reaction depends on mixing by transport processes, as well as the chemical composition of the pore fluid and the solid phase. In many cases, the microbes catalyze the reaction so that the reaction rates also depend on the abundance and activity of the microbes, the absence of toxic substances, and the provision of sufficient substrate as an energy and carbon source [Fetter 2008].

Under certain conditions, some reactions can successfully stop the spread of a contaminant or even contribute to its removal. In this context, natural attenuation, reactive barriers [Obiri-Nyarko et al. 2014], and enhanced bioremediation [Scow and Hicks 2005] are established remediation techniques that can effectively clean up groundwater with minimal technical effort. In such a dynamic and heterogeneous system as the subsurface, a constant monitoring of the environmental conditions is required to ensure that the reaction of interest is successfully sustained preventing further contamination of groundwater resources.

Challenges in reaction monitoring Quantifying transport, possible retardation and (bio)degradation processes of contaminants in groundwater is challenging. They are subject to spatial and, in the case of changing environmental conditions, temporal variability that hinder precise predictions of aquifer scale fate [Li et al. 2017].

The spatial extent of processes cannot be observed directly but must be inferred from indirect measurements, e.g. breakthrough curves at single observation points, destructive methods (drillings, core extraction) or laboratory experiments that are then extrapolated to the whole area of interest [Werth et al. 2010]. Due to the heterogeneity of the subsurface, this leads to an often non-unique process interpretation and thus a high uncertainty when information from small-scale point measurements is up-scaled to larger scale. This is already observed in the case of non-reactive water transport in sands [Barth et al. 2001]. To prove that a reaction is taking place, concentration measurements at single points are not sufficient, as they might also be influenced by dilution, and hence several lines of evidence, e.g. through isotope data, molecular biological data or models are required [Scow and Hicks 2005].

Moreover, not only the spatial variability and accessibility limits the process quantification, but it is also challenging to capture temporal dynamics. In the case of reactive barriers, where the retention relies on sorption of the contaminant, it is difficult to predict when the loading capacity of the material is reached. Downstream measurements will only show a signal once the contaminant breakthrough has already happened, a situation that the barrier is aiming to prevent. For the understanding of microbially-mediated reactive processes in the subsurface and their monitoring in space and time, proxies for microbial activity and their adaptation to a specific process are key. Traditional methods for the quantification of the microbial community evolution and activity rely on destructively-sampled sediment samples because 80% to >99.9% of the bacteria in groundwater stick to the sediment surfaces and don't float in the mobile water phase [Griebler and Lueders 2009; Mellage et al. 2015], a limitation that is already a challenge for small scale lab experiments.

1. Introduction

Filling the data gap: Reactive Transport Models One "traditional" way to deal with the data scarcity and limited access to the subsurface is to combine theoretical knowledge on the reactive processes with data into a numerical reactive transport model (RTM) [Li et al. 2021; 2017]. RTMs allow us to put our qualitative hypotheses on the reactive system to the test and to identify data gaps that are needed to prove whether a reaction is really occurring. RTMs also enable the quantification of reaction rates, to make predictions of the future behavior and on the effect of different environmental factors on the reaction rates [Li et al. 2017]. However, it is a challenge to find a RTM that is complex enough to describe the key processes, yet simple enough to be computationally affordable and constrained by data [Li et al. 2021]. Parameter estimation of RTMs can be a challenge and the lack of data on the solid phase and microbial dynamics can impede the discrimination of different processes or the accurate prediction of concentration changes in the future. While RTMs are powerful to combine single measurements into a cohesive representation of the subsurface and for quantitative rate predictions, they are not suitable as fast online monitoring tools. Acquiring a sufficient amount of data and the time needed for sampling and sample analysis plus choosing the appropriate model and its parameter estimation requires careful and time-consuming work flows.

Filling the data gap: Hydrogeophysics Geophysical methods are non-invasive and can provide information on the subsurface at a much higher spatial and temporal resolution than traditional methods [Rubin et al. 2005]. For the monitoring of reactions, the geophysical method of choice should be sensitive to the reaction of interest, e.g. through sensitivity towards alterations of the pore water chemistry, the surface chemistry, change in pore structure and the activity of microbes. Yet it should be specific enough to not be influenced by other parameters that vary in space and time independently of the reaction. To extend the application of geophysics from providing high-resolution data for RTMs towards an online monitoring method of subsurface reactions, requires fast data-acquisition and processing in combination

2. State of the art: SIP as a monitoring tool?

with a stand-alone interpretation in the absence of a complete picture of on site geochemistry. The geoelectrical method spectral induced polarization (SIP) has shown to be the most promising option of choice with respect to the monitoring of reactions [Kessouri et al. 2019]. In this thesis I explore its potential as an online monitoring method, filling the data gap of geochemical samples to improve our prediction of reaction dynamics.

The structure of the thesis In section 2, State of the art, I give an overview on the background of the SIP method and how it is currently used to monitor reactions. The objectives of this thesis, building and extending on the current knowledge are provided in section 3. Section 4, results and discussion, is divided into three parts in which I focus on different aspects of reaction monitoring using SIP. Finally, section 5 provides a cohesive summary and conclusion based on all parts of this thesis. It ends with an outlook on how this thesis contributes to future applications of SIP and which research directions are promising to fill remaining knowledge gaps.

2. State of the art: SIP as a monitoring tool?

The electrical double layer Minerals and organic matter (OM) form the solid phase of the subsurface. They possess charged groups at the interface with the pore water. These charges are mostly the result of pH-dependent (de)protonation reactions of hydroxyl and carboxyl-groups or a permanent charge due to the replacement of cations in the crystal lattice by other cations of lower valence. At circumneutral pH, both processes cause an excess of negative charges for most minerals and OM [Amelung et al. 2018]. In the adjacent pore water, counter ions are attracted towards the surface while ions of the same charge are repelled, causing the formation of the so-called electrical double layer (EDL). The EDL consists of the Stern layer, in which ions with opposite charge to the surface charge that are assumed to be tightly bound to the surface, and the diffuse layer which extends into the pore space. In the diffuse layer the concentration of counter ions decreases with distance to the surface until

2. State of the art: SIP as a monitoring tool?

the bulk concentration in the pore water and electroneutrality are reached. It can extend up to several nm into the pore water [Adamson and Gast 1997]. A schematic drawing of the EDL is shown in figure 2.1 (a). In the diffuse layer the bounding of the counter ions is expected to be solely through electrostatic forces. In contrast, counter ions in the Stern layer are additionally bound to the surface through chemical complexation [Amelung et al. 2018]. If an external electrical field is applied to a porous medium, the mobile charged ions in the pore space and in the EDL migrate in the direction of the electrical field. In the case of the EDL, where the direction of migration is limited to a tangential movement along the surface and against the electrostatic attraction of the surface charges, this process is called electrochemical polarization (see below). Because the EDL is dependent on properties of the solid phase and the pore water composition, signals obtained by SIP are affected by polarization processes so that SIP synchronously gains information on both the solid phase and the pore water, thus adding additional information to direct-current geo-electrical measurements [Revil et al. 2012b].

Basics of spectral induced polarization SIP is an active, four-point electrode method in which an alternating current is injected at different frequencies in the mHz to kHz range [Marshall and Madden 1959]. Due to its sinusoidal shape, the alternating current I [A] can be expressed by $I = I_0 e^{i\omega t}$, with the imaginary unit $i = \sqrt{-1}$, the angular frequency ω (rad) and the time t (s). The potential U [V] within the electric circuit is linked to the current I through Ohm's law ($U = R \cdot I$, with the resistance R [Ω]) and is thus also changing sinusoidally over time. Some components within the electric circuit, referred to as capacitors or inductors, store electrical charge. They built up an electric or magnetic field, respectively, causing a time lag between the injected current and the measured potential, the phase shift Φ [rad]. Since the complex exponential function can also be expressed by a real and an imaginary component, the complex current can also be expressed as:

$$I = I_0 \cdot \cos(\omega t) + i \cdot I_0 \cdot \sin(\omega t) = I' + i \cdot I'' \quad (1)$$

2. State of the art: SIP as a monitoring tool?

with I' being the real (in-phase) component and I'' being the imaginary (out-of-phase) component. It is convention in alternating current electrics to express current, potential and resistance (then referred to as impedance Z [Ω]) as complex quantities to account for the periodically changing electrical field. This has the advantage that the properties of the electrical circuit that determine electrical conduction through it are expressed by the real part and components that store electrical charge are expressed by the imaginary part of the impedance Z .

In an SIP measurement, the current is injected through an electrode pair and the resulting potential difference is recorded at a second electrode pair (thus SIP is referred to as four-point electrode method). In addition, the phase shift between the injected current and resulting potential is recorded. Using Ohm's law, the measurement yields the impedance magnitude Z_0 [Ω] plus the phase shift $-\Phi$ [rad] as raw measurements. They are then usually expressed in the complex-valued conductivity notation:

$$\sigma^* = \sigma_0 \cdot \exp(i \cdot \Phi) = \sigma' + i \cdot \sigma'' \quad (2)$$

where σ' is the real part of the complex conductivity [Sm^{-1}] and σ'' is the imaginary conductivity [Sm^{-1}] and σ_0 is the magnitude of the conductivity [Sm^{-1}]. Since the conductivity is the inverse of the resistivity ρ^* , σ_0 can be determined from the impedance magnitude Z_0 using an electrode-array dependent geometrical factor k [m]:

$$\sigma_0 = \frac{1}{k \cdot Z_0} \quad (3)$$

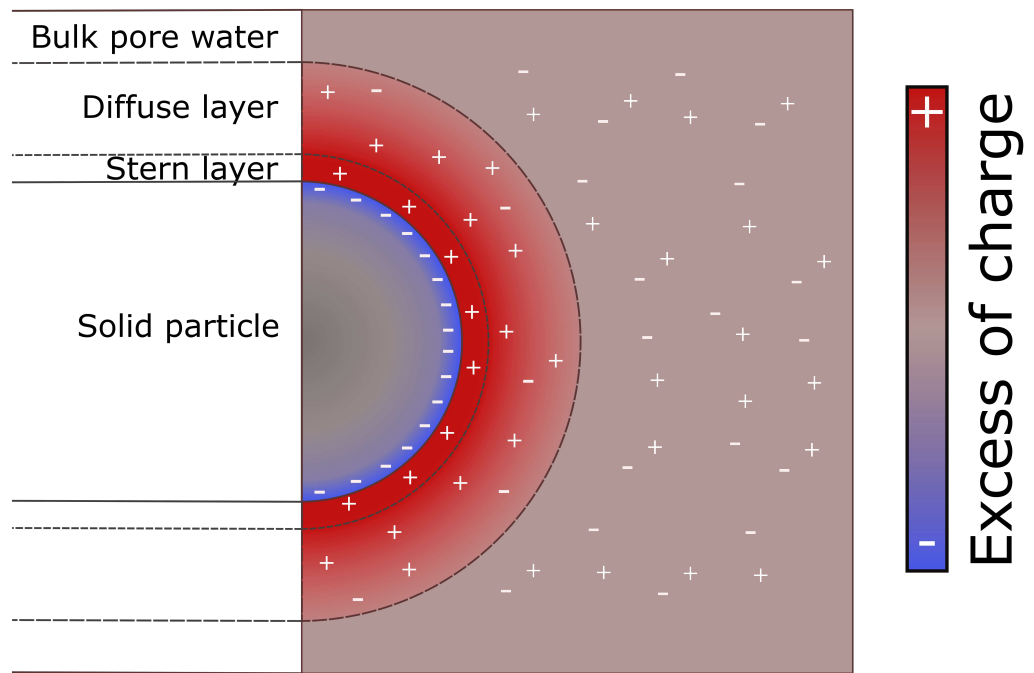
Note: The phase shift Φ of the complex resistivity ρ^* is negative, while it is positive for the complex conductivity σ^* , but has the same absolute value [Revil et al. 2012b]. In the following, the phase shift related to the complex conductivity, i.e. $\Phi > 0$, is shown.

The complex-valued conductivity σ^* is the apparent material property that determines electrical conduction and charge storage within the measured medium. It depends on (1) the electrical conduction through the pore fluid and along the surfaces and (2) a reversible storage of charge that is related to the electrochemical

2. State of the art: SIP as a monitoring tool?

polarization of the EDL [Kemna et al. 2012; Binley and Slater 2020]. The complex-valued notation allows to separate electrical conduction (σ') and charge storage (σ'') (through 'capacitors' in the subsurface): In the mHz to kHz range, the real conductivity σ' is hardly affected by the small phase shifts in the mrad-range. It is almost identical to the direct current (DC) conductivity, σ_0 , and mainly depends on the electrical conductance, σ_{el} , of the pore fluid through connected pores and, to a smaller extent, on electrical conduction along the grain-fluid interface, σ_{surf} [Slater and Glaser 2003]. The imaginary conductivity σ'' is of much lower magnitude than σ' and exhibits a frequency-dependent behavior related to polarization mechanisms of the EDL. Because the properties of the EDL depend on both, the surface properties and the pore fluid composition, σ'' is also sensitive towards changes in both parts of the subsurface.

(a)



(b)

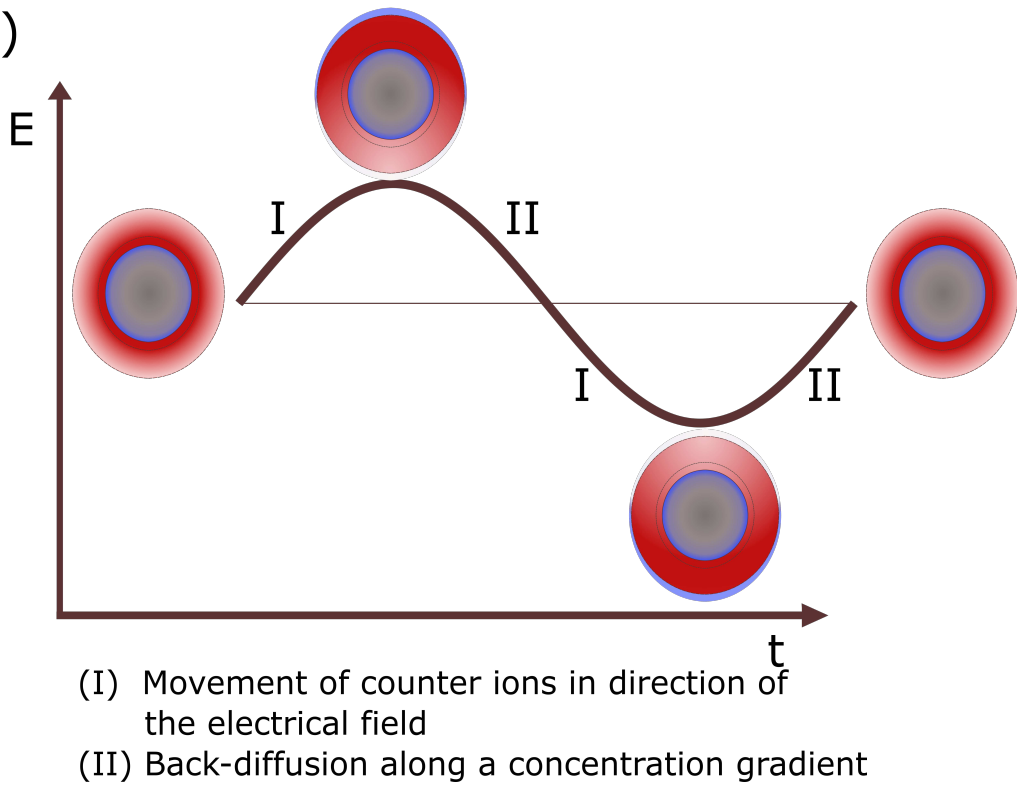


Figure 2.1: (a) Schematic representation of the electrical double layer (EDL) around a spherical particle. (b) Electrochemical polarization of the EDL during the application of an alternating electric field. Forces I and II act at the same time but the dominance of one over the other changes with time.

2. State of the art: SIP as a monitoring tool?

Electrochemical polarization In the low frequency range (mHz to kHz), electrochemical polarization of the EDL is the controlling polarization mechanism in porous media in the absence of conductive particles [Bücker et al. 2019]. Electrochemical polarization describes the effect of an external field on the migration of ions in the EDL and the subsequent back-diffusion once the external field is switched off [Leroy et al. 2008; Lesmes and Morgan 2001; Schwarz 1962]. In the context of this work, I will focus on the concept of electrochemical polarization around single grains as a model for EDL polarization and neglect the effect of membrane polarization, i.e. the electrochemical polarization due to a difference in ion mobility across pore throats and pore constrictions. The reactions that I monitor do not alter the pore network and hence I assume across all studies that the change of σ'' is controlled by changes in the EDL rather than the pore network. Further information on membrane polarization, as well as polarization effects due to conductive particles or at interfaces with different properties have been described e.g. by Binley and Slater [2020].

Figure 2.1 (b) schematically shows the polarization of the EDL around a spherical grain in an alternating electric field. The movement of ions in the direction of the electrical field causes a concentration gradient that points in the opposite direction and results in back-diffusion once the electrical field is reduced or switched off. In the context of electrochemical polarization around single grains, it is under debate whether polarization solely depends on the Stern layer or whether the diffuse layer needs to be accounted for as well. Stern layer polarization models coupled to surface complexation models successfully predicted the polarization response of glass beads and clay minerals [Leroy et al. 2008; Leroy and Revil 2009; Jougnot et al. 2010], arguing that in porous media the diffuse layers of adjacent particles overlap so strongly that polarization is being suppressed [Leroy et al. 2008]. However, other models account for the polarization of the entire EDL [Lesmes and Morgan 2001; Bücker et al. 2019] and hypothesize that the continuity of the EDL and thus the degree of compaction of the sediment determines the relative importance of the Stern and diffuse layers [Bücker et al. 2019]. In loosely compacted sediment as used in

2. State of the art: SIP as a monitoring tool?

this study, the Stern layer polarization most likely dominates the signal response.

In either case, the surface properties and the composition of the EDL pose a direct influence on the σ'' signal: In general, an increase in ionic strength will cause an increase of counter ions close to the surface that can polarize [Weller and Slater 2012]. Also, an increase in surface charge results in a higher concentration of counter ions in the Stern and diffuse layer and consequently an increase in σ'' [Hao et al. 2015]. Based on the surface polarization models there is a linear relationship between σ'' and the surface site density, a function of the cation exchange capacity (CEC) and surface area [Leroy et al. 2008; Leroy and Revil 2009; Revil and Skold 2011]. In systems with different ions, their different surface mobility, a property that depends on the strength of the attractive forces between surface and ion (i.e. the valence of the ion plus potential complexation bonds formed with the surface) will alter σ'' [Schwarz 1962]. Ben Moshe et al. [2021] showed how the replacement of monovalent cations by divalent cations reduced σ'' , due to their difference in surface mobility. Finally, the frequency-dependent magnitude of σ'' is a function of the length scale of polarization, that is, it depends on the particle or pore size [Scott and Barker 2003; Titov et al. 2002; Weller and Slater 2019]. The sensitivity towards various subsurface properties highlights the potential of SIP as a reaction monitoring method and demonstrates the challenges that might be associated with parallel signal contributions at the same time.

Polarization mechanisms of organic matter and microbes OM and microbes, just like most minerals, carry a negative charge on their (cell) surface and are thus, in a first approximation, expected to be surrounded by an EDL similar to the EDL forming around a mineral grain with the cell membrane acting as an electrical insulator between the cell interior and exterior [van der Wal et al. 1997; Amelung et al. 2018]. Therefore, organic constituents of the subsurface can be conceptualized as additional particle components undergoing electrochemical polarization and should affect the complex conductivity in a specific frequency range that resembles their

2. State of the art: SIP as a monitoring tool?

distinct polarization length scale.

Indeed, bacterial cells induce a polarization and the imaginary conductivity has been linked to microbial abundance and growth not only in cell suspensions [Zhang et al. 2014; Rosier et al. 2019], but also in low-polarizing background matrices like glass beads and quartz sand [Abdel Aal et al. 2010; Davis et al. 2006; Mellage et al. 2018]. Revil et al. [2012a] developed a model of microbial Stern layer polarization, analogous to the polarization of clay minerals, based on the cation exchange capacity of bacteria in which they found a linear relationship between biomass and σ'' , a finding that is also supported by experimental studies [Abdel Aal et al. 2006; Zhang et al. 2014]. .

In the case of organic matter, studies in peatlands have shown strong σ'' signals [Ponziani et al. 2012; Katona et al. 2021; Comas and Slater 2004] that show potentially strong polarization processes happening on OM. However, experiments at lower OM contents and in sediments where OM and the mineral constituents may interact, showed conflicting results [Schwartz and Furman 2014; Mellage et al. 2022b].

It is clear that, the surface structure of both cells and OM is substantially different from mineral grains. In the case of microbes, the interface between a cell membrane and the surrounding medium is certainly rather a three-dimensional body composed of a variety of bio-polymers [Poortinga et al. 2002] protruding into the extra cellular medium than a sharp transition as one would expect from mineral surfaces. The 3D polymer structure, that can also be expected for OM [Koopal et al. 2001], will affect the mobility of the surrounding counter ions. It is also known that a large fraction of the cell membrane proteins, that can form up to 60 % (w/w) of the cell membrane, are involved in energy transducing processes [Konings et al. 2002]. During the energy metabolism of cells, an electric potential of some mV, called membrane potential, between the extra cellular matrix and the cytoplasm [Alberts 2015] builds up. It is formed by a gradient of either H^+ , Na^+ or K^+ ions across the cell membrane [Lanyi 1979]. Hence, microbes can actively influence this gradient through their cell proteins [Konings et al. 2002; Alberts 2015] and are therefore also actively influencing

2. State of the art: SIP as a monitoring tool?

the composition of the surrounding fluid. Their polarization may therefore not only be a function of their abundance but also their metabolic activity, which was indeed observed as a drop in the σ'' and shift in the relaxation time during nitrite intoxication by Mellage et al. [2019].

Sensitivity towards different reaction types The electrochemical polarization mechanism provides the basis to understand how the σ'' signal is affected by different reactions. To estimate the sensitivity of σ'' towards the reaction of interest, it is important to differentiate between different reaction types. Figure 2.2 gives an overview on how four important reaction types can affect the σ'' signal. The reactions are differentiated on whether they involve only reactants in the aqueous phase (reactions of dissolved compounds), the exchange of compounds between bulk water and EDL (sorption), the formation of a new mineral phase (precipitation) or the reaction with a non-aqueous phase liquid (e.g. hydrocarbons). Many reactions in the subsurface are microbially-mediated, they require the presence of the microbes that are able to catalyze the reaction. In that case, the sensitivity of SIP towards microbial abundance and activity can influence σ'' .

2. State of the art: SIP as a monitoring tool?

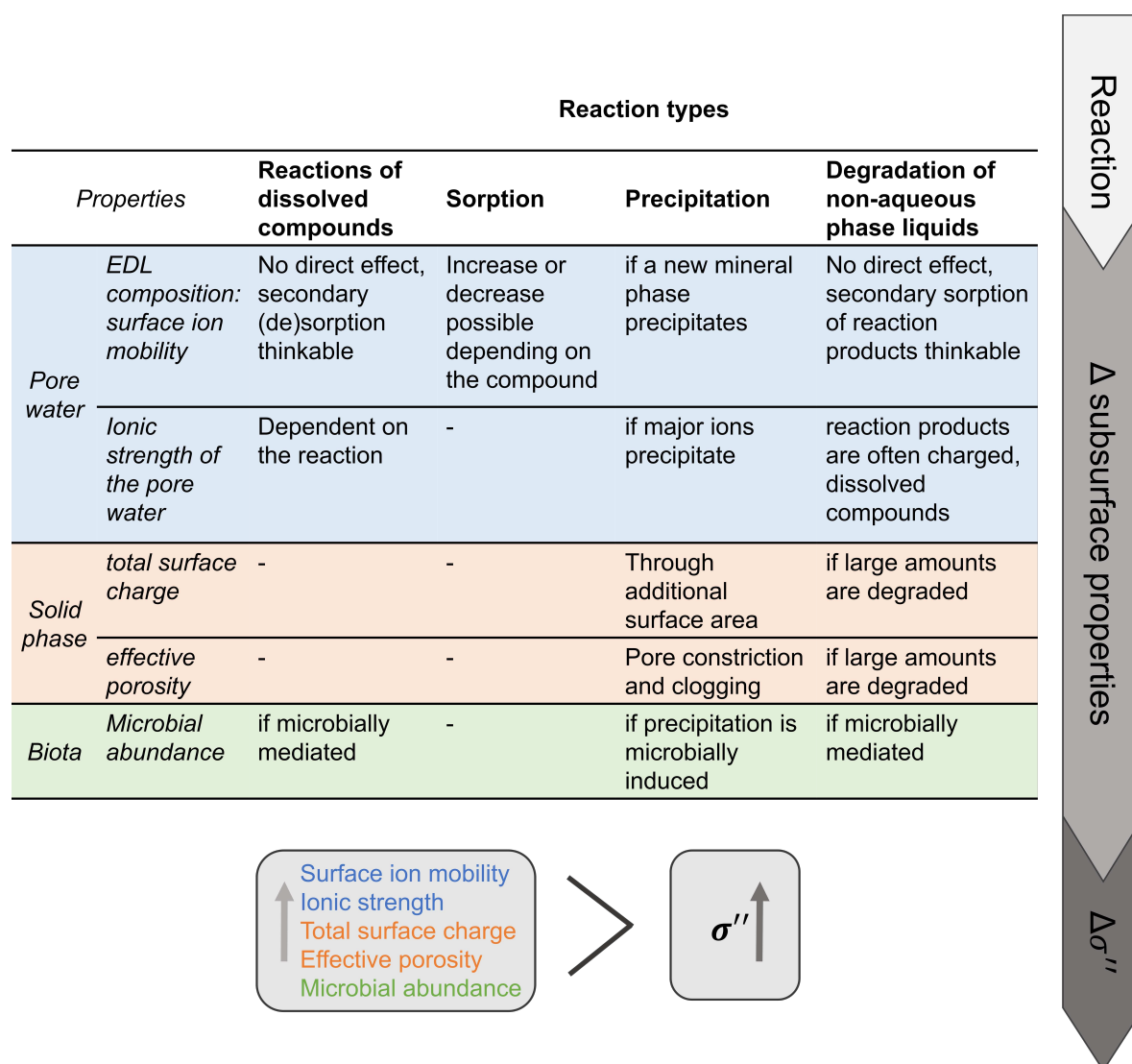


Figure 2.2: Reactions in the subsurface can be categorized into reaction types that affect subsurface properties in different ways. The figure provides an overview of the effect of different reaction types on subsurface properties and how a change in a specific subsurface property changes the σ'' signal.

SIP has been successfully used to study a series of different reactions. Nitrate reduction in sands [Mellage et al. 2019; 2018], hydrocarbon degradation [Abdel Aal et al. 2004; 2006; Kimak et al. 2019], bacterial growth in a saline environment [Joo et al. 2021] and microbially induced calcite [Saneiyan 2019] and sulfide [Williams et al. 2009; Ntarlagiannis et al. 2005] precipitation were investigated at the column scale, highlighting its potential to serve as a monitoring tool for a variety of

2. State of the art: SIP as a monitoring tool?

microbially-mediated processes of different reaction type. Also abiotic reactions, such as sorption of different heavy metals [Bate et al. 2023; Hao et al. 2022; Rahmani et al. 2024] and organic pollutants [Mellage et al. 2022a;b; Ben Moshe and Furman 2022], cation exchange processes [Ben Moshe et al. 2021; Vaudelet et al. 2011], the removal of non-aqueous liquids with surfactants [Deng et al. 2020] or precipitation of calcite [Placencia-Gomez et al. 2022; Izumoto et al. 2022] have been studied with SIP.

The sensitivity of SIP towards so many different reaction types and reactions demonstrates its versatility as a non-invasive method for the monitoring of reactions. Yet, it simultaneously demonstrates the challenge of the non-uniqueness of interpreting SIP signals. Several processes can happen at the same time or change in space and can thus impede or complicate the signal interpretation. Good, transferable approaches and workflows to deal with these ambiguities are required to transfer the knowledge gained in very controlled experiments towards "real-world" conditions.

Data acquisition and processing for online monitoring Reaction monitoring with SIP results in datasets containing a temporal, a frequency and a spatial dimension. In order to be applied as a online monitoring method, the data acquisition and data processing need to be as straightforward and automated as possible while reducing the dimensionality of the data to an extent where it can be directly interpreted yet keeping as much information as possible. In this context, I solely focus on 4-point electrode measurements assigning their measured value to the center of the potential electrode pair as a point measurements in space in this thesis. By doing so, inversion [Günther and Martin 2016] of the data is not needed as this would increase data processing and curation steps.

Phenomenological models, as the Cole-Cole relaxation model [Cole and Cole 1941; Pelton et al. 1978] are often applied to σ'' data to summarize the frequency-dependent behavior via a few characteristic parameters:

$$\rho^* = \rho_0 \cdot \left(1 - m \cdot \left(1 - \frac{1}{1 + (i \cdot \omega \cdot \tau)^c} \right) \right) \quad (4)$$

2. State of the art: SIP as a monitoring tool?

where ρ^* [Ωm] is the complex resistivity, ρ_0 [Ωm] is the direct-current (DC) resistivity, m_i [-] is the chargeability, ω [rad] is the angular frequency, τ [s] is the time constant related to the peak frequency and c , [-], is the Cole-Cole exponent that describes the broadness of the peak. Such models can be particularly helpful to analyze spectral data sets over time as they allow to quantify changes in spectral shape and peak frequency. Additionally, the polarization length scale can be estimated from the time constant. The frequency dependence of electrochemical polarization mechanisms is related to the diffusion coefficient of the ions in the EDL, D [m^2s^{-1}] and the length scale l [m] over which they polarize and can be approximated for spherical particles by [Schwarz 1962]:

$$\tau = \frac{l^2}{8 \cdot D} \quad (5)$$

where $\tau = \frac{1}{f}$ [s] is the relaxation time. Cole-Cole models assume an almost Gaussian distribution of σ^* in the frequency domain. In reality this condition is not always met, several signal contributions or measurement errors may impede a good fit of the model to the data. To overcome this issue, Debye decomposition methods [Bérubé et al. 2017; Weigand and Kemna 2016] that assume a distribution of relaxation times instead of one single τ can be applied. However, they do not reduce significantly the data to a set of a few parameters but to several parameter sets.

The different options to represent time-lapse SIP data have led to inconsistent data presentation and interpretation between different studies, making it difficult to compare data sets and to find common features. Experimental studies link either σ'' at a fixed frequency [Davis et al. 2006; Katona et al. 2021; Saneiyan et al. 2020; Bate et al. 2023], the σ'' maximum [Mellage et al. 2018; 2019; Zhang et al. 2014], the phase maximum [Flores Orozco et al. 2011; 2020; Katona et al. 2021; Saneiyan 2019; Vaudelet et al. 2011] or Cole-Cole fitted chargeability and relaxation time values to biogeochemical data [Mellage et al. 2019; 2022a]. Some also report relative changes in σ'' or σ' and relate these relative changes to relative concentrations or biogeochemical processes [Abdel Aal et al. 2010; Rosier et al. 2019; Mellage et al. 2019; Ben Moshe et al. 2021]. With the exception of Cole-Cole parameters fitted

2. State of the art: SIP as a monitoring tool?

to spectra and time-lapse presentation of spectral data sets, spectral information is disregarded or only specific time-points are selected to compare single spectra. Nevertheless, spectral information has the potential to enable the separation of parallel processes with different relaxation times. With more studies in different settings being presented and with an increasing interest in using SIP as a diagnostic tool, there is a need for comparability between different studies. Quantitative relationships between different reactive processes and one representation of changes in σ'' are required to identify common features across experiments and how other parallel signal contributions and system specific background can be identified and accounted for.

3. Objectives

This thesis aims at investigating the potential of SIP as a (online) monitoring method for the monitoring of reactions in porous media and to address some of the key issues that currently hinder its application. By investigating different aspects of reaction monitoring with SIP, I develop a framework on how and under which conditions SIP is a suitable online monitoring method that can refine the timing or location of traditional sampling events through a non-invasive observation of the duration and spatial extend of a reaction.

Most studies related to the relationship between specific reactions and SIP have been conducted under very controlled conditions, with glass beads, sand, commercially available minerals, or activated carbon. In order to close the gap between "real-world" applications and current research, I conduct experiments under close-to-natural conditions with sediment mixtures and groundwater as the pore water. The influence of OM on the SIP signal and its polarization mechanism has remained an open research question so far, yet it is involved in many (particularly nutrient-cycling) reactions [Amelung et al. 2018]. For microbially-mediated reactions the sensitivity of SIP towards changes in the presence of other polarizing components is unknown. Therefore, I focus on the SIP signal of microbes and OM during cation-exchange and nitrate reduction.

In order to meet these objectives, I conducted three research projects, presented in the Results and discussion section. *Part I: Background polarization of organic matter - Why solid organic matter matters in induced polarization measurements* addresses whether organic matter possesses a strong enough polarization signal to be relevant in sediment mixtures and whether the knowledge on electrochemical polarization of mineral surfaces can be transferred to organic matter. The work of this chapter has been published by Strobel et al. [2023b], Publication 2 in the Appendix. In *Part II: Monitoring of abiotic cation exchange - towards online monitoring with SIP* I investigate how the information content from processing SIP data can be maximized. Additionally, I investigate, whether σ'' measurements can serve as a proxy for sorbed

3. Objectives

concentrations in RTMs that are otherwise not accessible and how the incorporation of them improves the determination of reaction parameters or could replace "traditional" geochemical samples. The work of this chapter has been submitted by Strobel et al. [2024], Publication 3 in the Appendix. Finally, *Part III: Distinguishing between biotic and abiotic reactions* addresses the sensitivity of SIP to monitor biotic reactions in natural sediments despite the low abundance of microbes compared to the concentration of other solid phase components. Furthermore, this part contains my investigation of how biotic contributions to the SIP signal can be distinguished from abiotic processes occurring in parallel. This chapter has been published by Strobel et al. [2023a], Publication 1 in the Appendix.

4. Results and discussion

4.1. Background polarization of organic matter - Why solid organic matter matters in induced polarization measurements

Understanding the geoelectrical properties of OM is important for hydro- and biogeophysical surveys in shallow OM-containing sediments, yet its relative influence on the complex conductivity compared to other soil components like clay minerals or pyrite has so far been unknown. A limited number of studies has shown promising, yet conflicting, results that SIP is sensitive to OM. Ponziani et al. [2012], Katona et al. [2021] and Comas and Slater [2004] investigated the IP signature of peats and peatlands. They observed a significant IP signal with phase shifts of several mrad that could originate from the OM but from their work it is not clear whether also the presence of sulfides [Ntarlagiannis et al. 2010] might cause such strong signals. Laboratory experiments on artificial mixtures of soil and OM at lower OM contents showed contrasting results: Schwartz and Furman [2014] observed a decrease of σ'' with an increase in OM content, whereas Mellage et al. [2022b] observed the opposite relationship. It was hypothesized by Katona et al. [2021] and Mellage et al. [2022b] that unknown polarization mechanisms that differ from the classical electrochemical polarization might be active in OM.

I quantified the relationship between the OM content and σ'' in sediment mixtures of calcite sand and peat and in field cores with a high variability of OM contents. The artificial sediment mixtures enabled me to cover the full range of OM contents, work with replicates and control the pore water chemistry. Because of the sedimentology of the site that I investigated, I chose calcite sand as the mineral matrix for the artificial mixtures to mimic the Tufa sediments of the field site. It's a holocenic freshwater carbonate that contains a highly varying OM content stemming from mm to cm scale peat lenses up to peat layers. Other polarizable minerals were absent in this system. In this first research project, I explored the applicability of EDL-based models for or-

4. Results and discussion

ganic surfaces and derive petro-, or rather, *organo*-physical relationships between the total organic carbon (TOC) content and σ'' . I presented the OM content as its TOC content that is the weight fraction of carbon in the total solid mass. Hence, the total organic matter content is higher than the TOC content (as the masses oxygen, hydrogen and other elements that form OM need to be added). Presenting the OM content as the TOC content has the advantage of TOC being a standard quantification technique for OM that allows to easily compare the results across samples and studies.

SIP measurements on peat-sand mixtures The complex conductivity measurements using artificial soil mixtures revealed a linear relationship between the TOC content and σ'' . The dataset spans over four orders of magnitudes from a trace amount of less than 0.01% in the pure calcite samples to 41% TOC in the pure peat and is shown in figure 4.1a as the relationship between the mean σ'' at 50 Hz and the TOC content of each sample column (red markers). The relationships in figure 4.1 are consistent across the measured frequency range, but are shown here at 50 Hz as this is the approximate peak frequency of the peat spectra. The pore-water composition (i.e., EC) was held constant in the experiment. Therefore, the σ'' -TOC relationship, with a 525-fold increase of σ'' compared to only a 4.4 fold increase in σ' (figure 4.1c) highlights the strong control of electrochemical polarization of OM on the magnitude of σ'' . The lower relative increase of σ' showed that electrolytic and surface conduction was also affected when replacing calcite sand with peat. Indeed, the porosity increased due to the addition of peat and the increase in σ' could be attributed to a better electrolytic conduction through the pore space in accordance with Archie's law (figure 4.1d).

Existing grain based models [Leroy et al. 2008; Jougnot et al. 2010; Revil et al. 2023] predict a linear relationship between σ'' and CEC for mineral surfaces that is also observed in this work for OM (figure 4.1b). Furthermore, the linear relationship between the CEC and σ'' suggests that polarization in these OM-containing sedi-

4. Results and discussion

ments is driven by processes analogous to electrochemical polarization of the EDL of mineral surfaces.

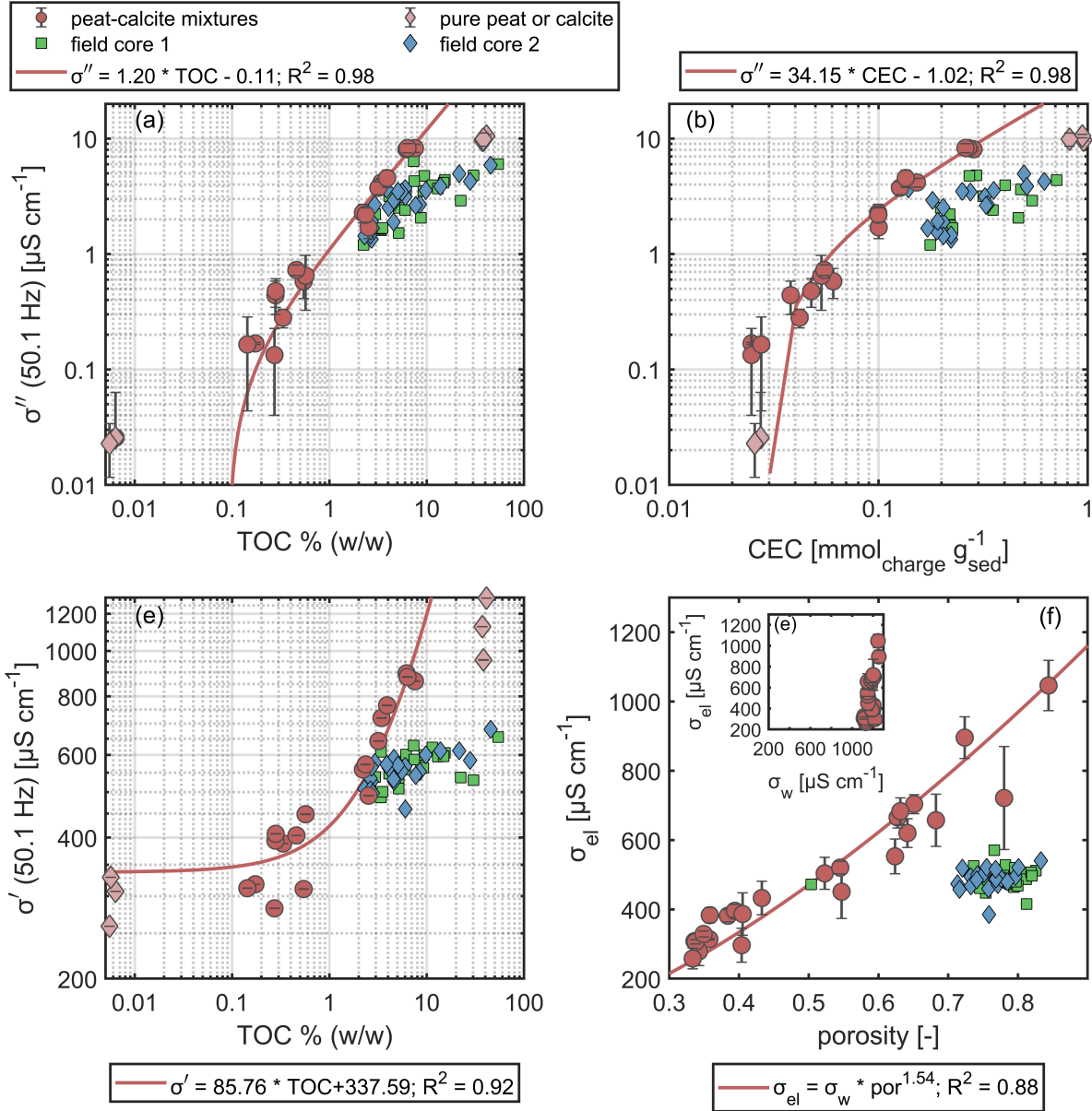


Figure 4.1: Polarization of organic matter: Fitted linear relationships between complex electrical conductivity and selected soil properties. (a) σ'' versus total organic carbon (TOC) content, (b) σ'' versus cation exchange capacity, (c) σ' versus TOC, (d) electrolytic conductivity versus porosity, (e) electrolytic conductivity versus pore water conductivity. Red markers: artificial peat-calcite mixtures; blue/green markers: measurements on field cores from the Tufa aquifer. Error bars for the peat-calcite mixtures show the standard deviation between the three measurements in one column. Note: Pure peat and pure calcite samples (diamond markers) were not considered for fitting the linear relationships for the peat-sand mixtures.

4. Results and discussion

Real-world case: Intact cores from Tufa sediments with peat layers The depth-resolved complex conductivity, TOC, CEC and porosity of two field cores with Tufa sediments align well with the trends revealed by the artificial peat-calcite mixtures. With depth, the TOC content ranged from 2.3 up to 56%, yielding an σ'' of 1.3 up to $5.5 \mu\text{S cm}^{-1}$. The field core measurements are shown in figure 4.1 as blue and green markers. Because of the higher intra-particle porosity of Tufa carbonates compared to calcite sand, the porosity showed a less pronounced increase with increasing TOC content and as a consequence the σ' increase also did show a lower increase with TOC for the field cores. Therefore, electrolytic conduction did not increase significantly. The Tufa sediments provide field samples that demonstrate how strongly the complex conductivity can be affected by OM also under field conditions.

On the importance of organic matter content in SIP surveys Based on the findings presented in the previous paragraphs, I demonstrate that SIP can delineate zones rich in OM, and that even low fractions of OM (TOC <1%) significantly alter the electrical properties of unconsolidated media. To prevent data-misinterpretation, the quantification of TOC should be an integral part of the sediment characterization for ground-truthing of (S)IP surveys, in particular, when interpreting data in soils or other OM rich porous media.

If needed, further investigation on the CEC of the sediment could then follow. I did not find evidence for another "non-classical" polarization mechanism as proposed by Katona et al. [2021] and Mellage et al. [2022b]. To date, the CEC can thus be regarded as the best predictor of OM polarization. With a CEC of $1.3 \text{ mmol}_{\text{charge}} \text{g}_{\text{sed}}^{-1}$, the OM used in this study is comparable to 2:1 clay minerals of very high CEC and considerably higher than 1:1 clay minerals [Carrol 1959]. The CEC varies from site to site, which is why the *organo*-physiscal relationship between σ'' and TOC that I derived cannot be directly applied to other field sites and site-specific quantifications of the CEC are required to estimate the relative importance of the OM.

4.2. Monitoring of abiotic cation exchange - towards online monitoring with SIP

In section 4.1, I show evidence that polarization on OM follows similar principles as electrochemical polarization on mineral surfaces. To put this to the test under dynamic, reactive conditions I compared the SIP response during flow-through experiments injecting different cations for a certain amount of time. I chose a monovalent cation (Na^+) and two divalent cations with different surface complexation strengths (Ca^{2+} and Zn^{2+}). The columns were filled with a calcite sand-peat mixture and Ca^{2+} -dominated pore water. In this system, I monitored the cation exchange reaction occurring as the injected cation $\text{C}_{\text{inj}}^{n+}$ replaces the background cation $\text{C}_{\text{bg}}^{m+}$ in the EDL of the OM:

$\text{C}_{\text{inj}}^{n+}(\text{aq}) + \frac{n}{m}[\text{C}_{\text{bg}}^{m+}-\text{OM}] \rightleftharpoons \frac{n}{m}\text{C}_{\text{bg}}^{m+}(\text{aq}) + [\text{C}_{\text{inj}}^{n+}-\text{OM}]$. It is a reaction that -in theory- solely alters the composition of the EDL while other subsurface properties (figure 2.2) are unaffected by it. Under these circumstances, the effect of the reaction on σ'' should be predictable based on the change in surface ion mobility induced by the cation exchange. Surface ion mobility describes the mobility of ions in the EDL in dependence on the attractive forces between surface and ion. Consequently, ions with a higher charge or ions that form complexation-type bounds with the surface have a lower surface ion mobility than those with a lower charge and no complexation interactions. Since the σ'' is directly proportional to the surface ion mobility [Revil 2012; Hao et al. 2015], I expected Na^+ as a monovalent, non complexing ion to increase σ'' , whereas Zn^{2+} as a divalent, complex forming ion [Randhawa and Broadbent 1965; Himes and Barber 1957] should cause a decrease of σ'' . Injecting a higher concentration of the background cation Ca^{2+} should not alter the surface ion mobility and thus σ'' strongly. Having a clear expectation on how the σ'' signal is affected by the reaction of interest is the prerequisite for online monitoring with SIP. Hence, these experiments enabled me to explore how SIP can be utilized for qualitative online monitoring. In addition, I investigated to which extent the incorporation of SIP data into reactive transport modeling frameworks can replace 'traditional' geo-

4. Results and discussion

chemical samples or improve the determination of reaction parameters.

Qualitative monitoring of cation exchange processes Figure 4.2 shows $\Delta\sigma''$ versus $\Delta\sigma'$ timeseries of the three cation injections at a single SIP measurement location. The arrival time, and pulse duration of the conservative, coinjected, anion Br^- was captured by $\Delta\sigma'$ (grey, dashed lines) in all cases [Ben Moshe et al. 2021]. Inline with the theoretically expected behavior for classical electrochemical polarization, the different surface ion mobilities of the three cations became directly evident from the different $\Delta\sigma''$ time series (colored lines), with Na^+ having the strongest increase of σ'' and Zn^{2+} showing a constant decrease of $\Delta\sigma''$ after an initial increase. This experiment provided further evidence that OM polarization is very comparable to electrochemical polarization of mineral surfaces. OM-free control columns did not show evidence for cation exchange taking place on the calcite sand and only a very low σ'' signal was recorded. Consequently, both the observed SIP signal and the cation reaction itself can be attributed to the OM in the system.

Until this point, I neglected the increase and decrease of $\Delta\sigma''$ at the beginning and end of the breakthrough that was observable in all three experiments. I attribute it to a change in electrical conductivity (EC) of the injected solution as NaBr , CaBr_2 or ZnBr_2 are added to the background solution and it raised the question whether and how the effect of surface ion mobility changes can be separated from a change in $\Delta\sigma''$ due to EC variations in the pore water.

4. Results and discussion

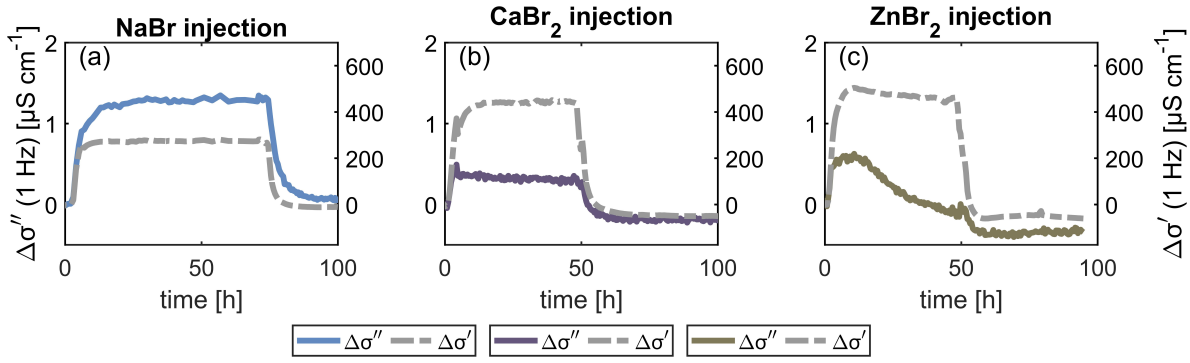


Figure 4.2: Comparison of the change in real and imaginary conductivity during the injection of different cations into OM containing columns: NaBr (a), CaBr₂ (b) and ZnBr₂ (c). The frequency of 1 Hz was chosen as it showed the lowest impact of electrode polarization effects on the data.

Removing electrical conductivity effects from the $\Delta\sigma''$ signal Separating the reactive, ion exchange driven component of $\Delta\sigma''$, $\Delta\sigma''_{IE}$, from the change driven by a change in EC, $\Delta\sigma''_{EC}$, required knowledge on the EC at the location and time point of the SIP measurements. As a proxy for EC, I used the concentration of the conservative anion Br^- at the midpoint of the potential electrodes. Br^- marked the beginning and end of the high-salt injection and the concentrations could be determined using a RTM calibrated to outflow measurements. Assuming a linear relationship between EC or $c(\text{Br}^-)$ and $\Delta\sigma''$ yields:

$$\Delta\sigma'' = \Delta\sigma''_{IE} + \Delta\sigma''_{EC} = \Delta\sigma''_{IE} + a \cdot c(\text{Br}^-) \quad (6)$$

in which a ($\mu\text{S L cm}^{-1} \text{ mmol}^{-1}$) is the linear proportionality constant between the aqueous concentration of bromide $c(\text{Br}^-)$ (mmol L^{-1}) at the midpoint of the potential electrode pair and $\Delta\sigma''_{EC}$. While Weller et al. [2011] found a power law relationship between between EC and σ'' , I chose a linear relationship primarily because of the small range over which EC varied in this experiment and to keep the amount of parameters as low as possible. This parameterization provided the first step for the direct coupling of SIP data and a RTM, that will be discussed in the next section.

Constraining solid phase concentrations - SIP and RTM In the case of Zn^{2+} , the qualitative monitoring using the $\Delta\sigma'' / \Delta\sigma'$ plots helped to identify zones of different

4. Results and discussion

reactivity (figure 4.3a-c). The ZnBr_2 injection resulted in a spatially variant trend in $\Delta\sigma''$ after the initial increase during the breakthrough of the conservative solute front. Closest to the inlet of the column (figure 4.3a), $\Delta\sigma''$ started to decrease whereas with increasing distance to the inlet this started later (figure 4.3b) or was not the case (figure 4.3c). I interpreted this as a sign for complete Zn^{2+} sorption in the first part of the column, where an effect on $\Delta\sigma''$ is observable. This agrees with the absence of Zn^{2+} in the outflow. The $\Delta\sigma'' / \Delta\sigma'$ plots shown in figure 4.2 condensed the information stemming from the multidimensional SIP measurements into a format that can be quickly evaluated and is thus valuable in the monitoring of column or other time-lapse experiments.

To transfer this qualitative interpretation into the RTM framework, the fraction of $\Delta\sigma''$ that is related to ion exchange, $\Delta\sigma''_{IE}$, was linked by a proportionality constant p_{inj} ($\mu\text{S g cm}^{-1} \text{ mmol}^{-1}$) to the concentration of the injected cation, s_{inj} (mmol g^{-1}) on the OM:

$$\Delta\sigma''_{IE} = p_{inj} \cdot s_{inj} \quad (7)$$

Combining equations 6 and 7, lead to a full parameterization of $\Delta\sigma''$ that could be used in the RTM framework to constrain the sorbed concentration s .

In figure 4.3a-d the fit of a RTM to the outflow concentration data and $\Delta\sigma''$ are shown for the Zn^{2+} injection. The ion exchange was described by competitive Langmuir sorption of the injected Zn^{2+} and the background ions Me^{2+} (combining Ca^{2+} and Mg^{2+} into one species for the modeling). The model predicted both data sets, concentration data and $\Delta\sigma''$ well. The decreasing effect of Zn^{2+} sorption on $\Delta\sigma''$ becomes evident from the separation of $\Delta\sigma''$ into the ion exchange and EC component. Testing the model performance with a different amount of model data, revealed that the SIP data were not able to fully replace the information on the background cations and using only a third of the concentration data ('reduced dataset') was sufficient to predict the outflow behavior even in the absence of the SIP data. That the addition of $\Delta\sigma''$ into the dataset did make a difference can be observed in the spatial profiles of sorbed Zn^{2+} concentrations (figure 4.3e). They are shown at the end of the Zn^{2+}

4. Results and discussion

injection. A Bayesian parameter estimation allowed to also estimate the uncertainty of the model fit, and the addition of SIP data to the dataset reduced the uncertainty of the sorbed concentrations as well as the uncertainty of some parameters (shown in section A.3) significantly. In agreement with the qualitative interpretation of $\Delta\sigma''$, the Zn^{2+} sorption was restricted to the upper part of the column in scenarios where the $\Delta\sigma''$ data were used for model calibration.

This research project is a proof-of-concept on how (S)IP data can be incorporated in reaction monitoring of reactions involving charged surfaces. Separating $\Delta\sigma''$ into a fraction caused by changes in EC from those caused by the reaction can enhance the interpretability of SIP signals in dynamic systems and facilitates the assessment of relative effects of different processes on $\Delta\sigma''$.

The incorporation of SIP data into reactive-transport modeling schemes has been proposed [Kessouri et al. 2019], however, to my knowledge, this was the first direct coupling of SIP data and a RTM that highlights the potentials and (current) limitations of the addition of SIP data in the model calibration. With the simple relationships in this work, I demonstrate how quantitative coupling may be implemented. Yet the additional information gained was limited, with the exception of a reduction of parameter uncertainty. SIP data couldn't fully replace concentration data of a reactive species in this experiment. In general, such a coupling could lead to more accurate and comprehensive models, helped identifying missing processes and thereby advanced our capability to monitor and interpret complex geochemical processes in situ.

4. Results and discussion

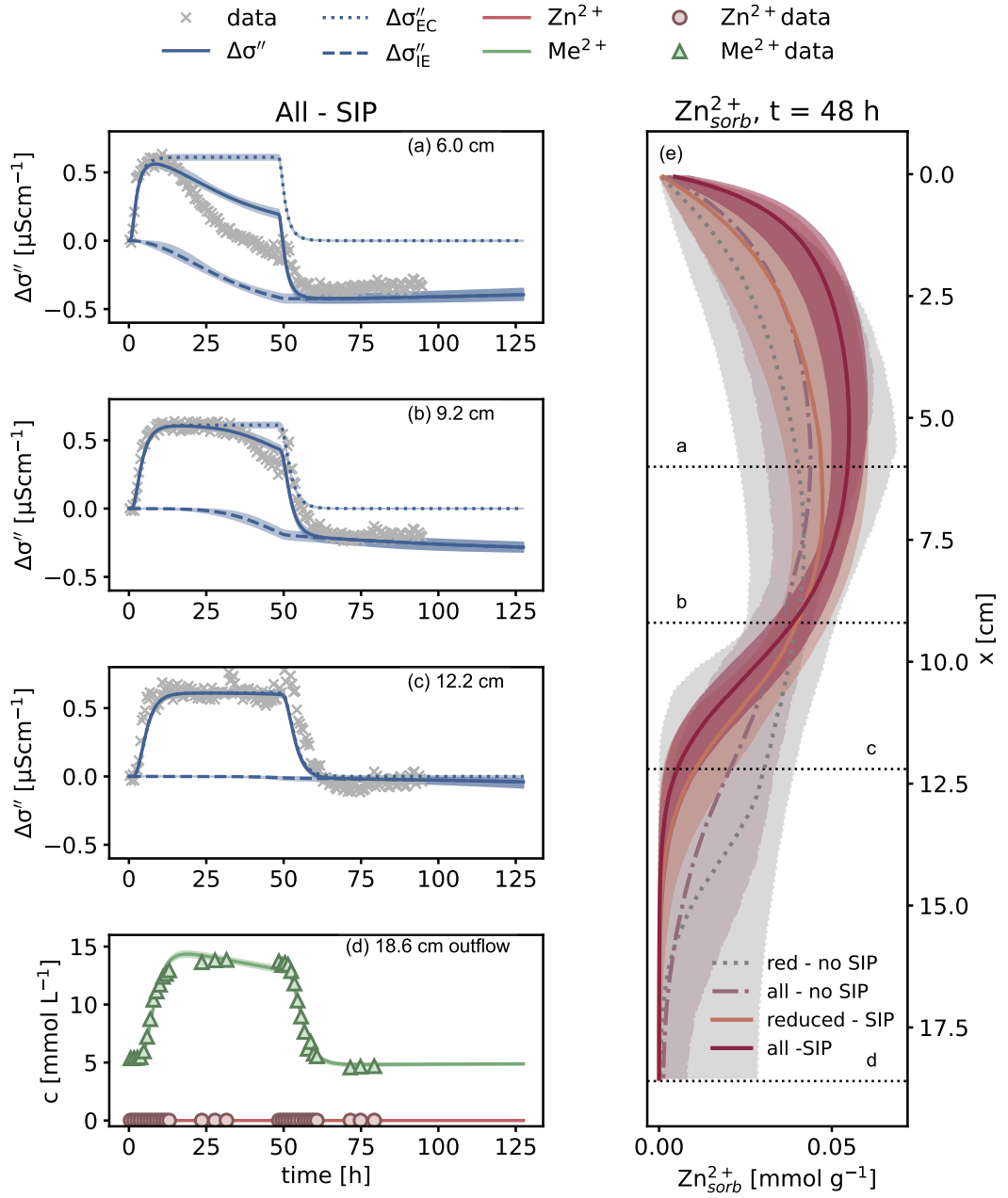


Figure 4.3: Model-data comparison of the simulation of the Zn^{2+} -experiment using all chemistry data (left column). Panels a – c show the comparison of the simulated $\Delta\sigma''$ compared to measured $\Delta\sigma''$ at all locations. In addition, the contribution of electrical conductivity, σ''_{EC} , and the ion exchange reaction, σ''_{IE} , to the overall change in σ'' are shown as dotted and dashed lines, respectively. In panel d the simulated concentrations are compared with the measured concentrations. Additionally, a profile of the simulated sorbed concentrations of Zn^{2+} at the end of the injection is shown for different parameter estimation scenarios (e). The dashed lines in panel denote the location of the SIP measurements and the outflow. The shaded areas show the range between the 5th and 95th quantile.

4.3. Distinguishing between biotic and abiotic reactions

Due to the ubiquitous presence of microbes and their unique role in catalyzing important reactions in the subsurface, a non-invasive monitoring of microbially-mediated reactions in natural, complex sediment mixtures would amplify the potential applications of SIP monitoring. For this, it is key to identify potential limitations in measurement sensitivity, and to find approaches to distinguish biotic from abiotic reactions that occur in parallel.

Natural sediments: A challenge for SIP measurement sensitivity? Despite growing evidence that SIP signals are affected by microbial abundance and activity, the unique attribution of SIP signals to microbial processes in natural sediments has not been investigated. In the presence of a polarizing background matrix it was unclear whether the sensitivity of SIP is sufficient to detect changes in a volume fraction of soils as small as that of microbial biomass. With denitrification, I chose a microbially-mediated reaction that did not involve changes in the mineral fraction of the sediments due to precipitation/dilution effects so that changes in σ'' can be attributed to the microbial activity and abundance itself. Heterotrophic denitrification is the microbial reduction of nitrate (NO_3^-) via several intermediates to N_2 , coupled to the oxidation of organic carbon stemming from the solid organic carbon fraction [Rivett et al. 2008b]. In part, denitrification was also chosen due to its environmental relevance [Abascal et al. 2022; Camargo and Alonso 2006] and the challenges that are associated with the quantification of denitrification rates and their monitoring in the field [Pinay et al. 2015; Groffman et al. 2006].

To monitor biotic reactions with SIP under controlled conditions, I stimulated microbial denitrification in an sediment with its indigenous microbial community by injecting nitrate into flow-through columns. The sediment originated from the same field site as the samples in section 4.1 and was rich in OM and calcite. A schematic of the experimental set-up and details on the experimental procedure can be found in the appendix A.1. The measured breakthrough curves were analyzed using a reac-

4. Results and discussion

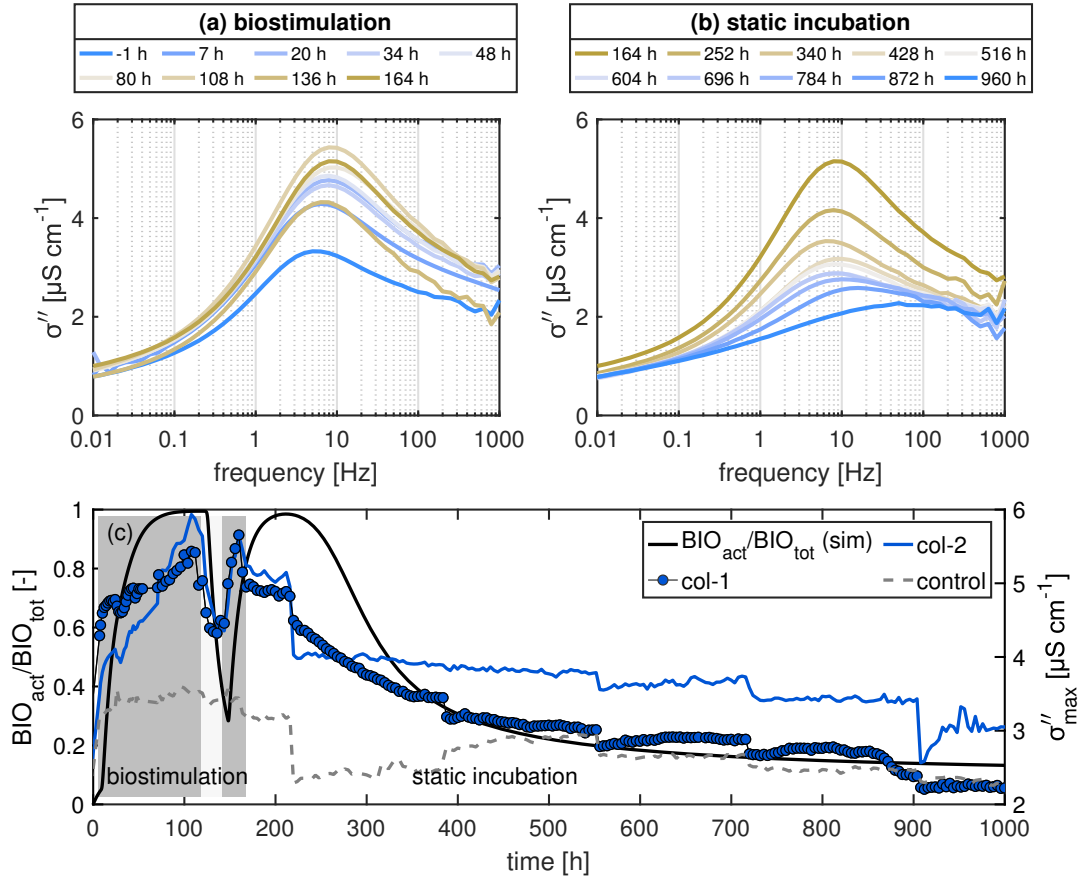


Figure 4.4: Selected spectra in column 1 (Col-1) during (a) the biostimulation phase and (b) the static incubation phase. The fraction of simulated active biomass is compared to the maximum imaginary conductivity, σ''_{max} , of both columns and the non-stimulated control at the same location in panel (c). The gray areas denote times in which NO_3^- was injected.

tive transport model to obtain time-series of microbial activity at different locations within the column. They served as a comparison to link σ'' signals to the denitrification reaction.

In figure 4.4a and b, σ'' spectra during the two phases of the experiment, namely the continuous injection of NO_3^- (i.e. biostimulation, 4.4a) and the incubation of the sediment under no-flow conditions until the nitrate in the pore water was replenished (i.e. static incubation, 4.4b) are shown. They highlight how the SIP signal increased during the biostimulation which disappeared again during the static incubation. During the phase of bioactivity, a different peak shape can be observed, compared to the background polarization that is recovered at the end of the static incubation phase.

4. Results and discussion

This points towards an additional polarization mechanism being active during the denitrification in addition to the background polarization. This additional polarization could be stemming from the microbes. To confirm this hypothesis, I simulated the fraction of active biomass based on the NO_3^- concentration data with a RTM. A comparison of the temporal evolution of active biomass with the maximum of σ'' in both columns revealed striking similarities across both phases (figure 4.4c) leading to the conclusion that we are indeed observing a microbial contribution to σ'' in a natural sediment.

Microbial activity or abundance? In natural sediments cell densities are relatively stable, but facets of the microbial community are known to become active in response to the presence or absence of substrates [Lennon and Jones 2011]. Based on electrochemical polarization and the ability of microbes to alter the chemical gradients across the cell membrane and the cell surface itself [Konings et al. 2002; Maloney et al. 1974], it is reasonable to assume that not only microbial abundance but also microbial activity influence σ'' . Due to the short time scale of the experiment, I did not expect major changes of the microbial abundance but rather in the microbial activity. In particular, I expected the microbial community to respond in metabolic activity but not in biomass to a short time of 23 h where no NO_3^- was injected (after 119 h) and consequently implemented a biomass activation term in dependence of the NO_3^- concentration based on a switch-function [Stolpovsky et al. 2011; Mellage et al. 2015] in the RTM. The effect of microbial activity on σ'' has not been investigated in literature except for a study in which a reduction in σ'' due to toxicity effects on microbes was observed [Mellage et al. 2019]. Furthermore, it is an aspect that has not yet been discussed in the context of experimental designs. However, it could explain the difference in σ'' magnitude between studies in the absence of substrates (and thus activity) [Zhang et al. 2014; Abdel Aal et al. 2010] of less than $1 \mu\text{S cm}^{-1}$ and in the presence of substrates [Joo et al. 2021; Mellage et al. 2018; Rosier et al. 2019] that were on the order of several $\mu\text{S cm}^{-1}$ analogous to this work. At this state,

4. Results and discussion

the relative effect of microbial abundance and activity remain unknown but this experiment suggested that σ'' might be strongly affected by the metabolic state, hence activity, of the microbes.

Superimposed polarization mechanisms: Separation of biotic and abiotic reactions The experiment was conducted in natural bicarbonate buffered groundwater to which NaNO_3 was added. As a consequence, a cation exchange reaction of Na^+ with the background ions Ca^{2+} and Mg^{2+} occurred synchronously some uncertainty remained on how strong the microbial contribution to σ'' was compared to the abiotic cation exchange reaction. Solely interpreting σ'' data at a single frequency, as shown in figure 4.4c could be misleading. Therefore, I developed a decomposition method to separate abiotic and biotic contributions to σ'' based on their difference in frequency-dependence.

Polarization due to a microbially-mediated reaction has a fundamentally different effect on the polarization than cation-exchange. While cation-exchange alters the EDL on all charged surfaces, an increase in microbial activity and abundance leads to a change of the "EDL" of a very specific fraction, the microbes. Hence, cation exchange acts on all polarization length scales and consequently on all frequencies, while biotic reactions alter the σ'' signal only in a limited frequency range that corresponds to the polarization length scale of microbes. To separate these two contributions to the signal, I applied a superposition of two Cole-Cole models (equation 4) to account for polarization stemming either from the sediment matrix or from the active microbial community, respectively:

$$\rho^* = \rho_0 \cdot \left(1 - \left(m_{mat} \cdot \left(1 - \frac{1}{1 + (i \cdot \omega \cdot \tau_{mat})^{c_{mat}}} \right) + m_{bac} \cdot \left(1 - \frac{1}{1 + (i \cdot \omega \cdot \tau_{bac})^{c_{mat}}} \right) \right) \right) \quad (8)$$

in which all terms have the same meaning as in the single Cole-Cole model (equation 4) but the subscripts "mat" and "bac" refer to the matrix- and bacterial-specific coefficients. In the following CC_{matrix} (CC = Cole-Cole) denotes the matrix-related contribution to polarization and $\text{CC}_{bacteria}$ the polarization induced by the microbial community. Cole-Cole model parameters have been shown to be highly correlated

4. Results and discussion

impeding parameter interpretation [Bérubé et al. 2017; Fiandaca et al. 2018]. By re-converting the parameters into complex conductivity values, ambiguities in parameter estimation can be reduced because a subset of parameters is interpreted jointly. The high correlation between the parameters also causes challenges during parameter estimation. For the two-term Cole-Cole model it was therefore necessary to constrain the single parameters based on prior knowledge. First, the matrix-related parameters τ_{mat} and c_{mat} had to stay close to the parameter of a single Cole-Cole model that was fitted to spectra obtained before the start of the experiment. Second, τ_{bac} was constrained to reported peak frequencies of bacteria in the range of 2 - 30 Hz [Mellage et al. 2019; 2018; Rosier et al. 2019; Zhang et al. 2014] and a Cole-Cole exponent c_{bac} greater than 0.5 ensured a narrow peak around the peak frequency. These constraints ensure that each polarization contribution maintains its frequency-dependent shape while it can change in magnitude.

Before and after the biostimulation, the Cole-Cole decomposition attributed the polarization to the matrix component, CC_{matrix} , only. Figure 4.5a shows the Cole-Cole decomposition at the end of biostimulation phase where it predicts that matrix and bacteria contribute to a similar extent to the overall magnitude of electrochemical polarization at the peak frequency of the bacterial polarization of 6 Hz. Plotting only the microbial contribution $CC_{bacteria}$ showed clearly, how microbial activity increased during the biostimulation (figure 4.5b) and then completely vanished again once all NO_3^- is consumed (figure 4.5c), while in the non-biostimulated control no microbial activity can be expected based on the SIP data. Thus, the Cole-Cole decomposition of the SIP response provided a means to quickly differentiate between zones and times of high bio-activity versus no bio-activity independent of concentration data.

4. Results and discussion

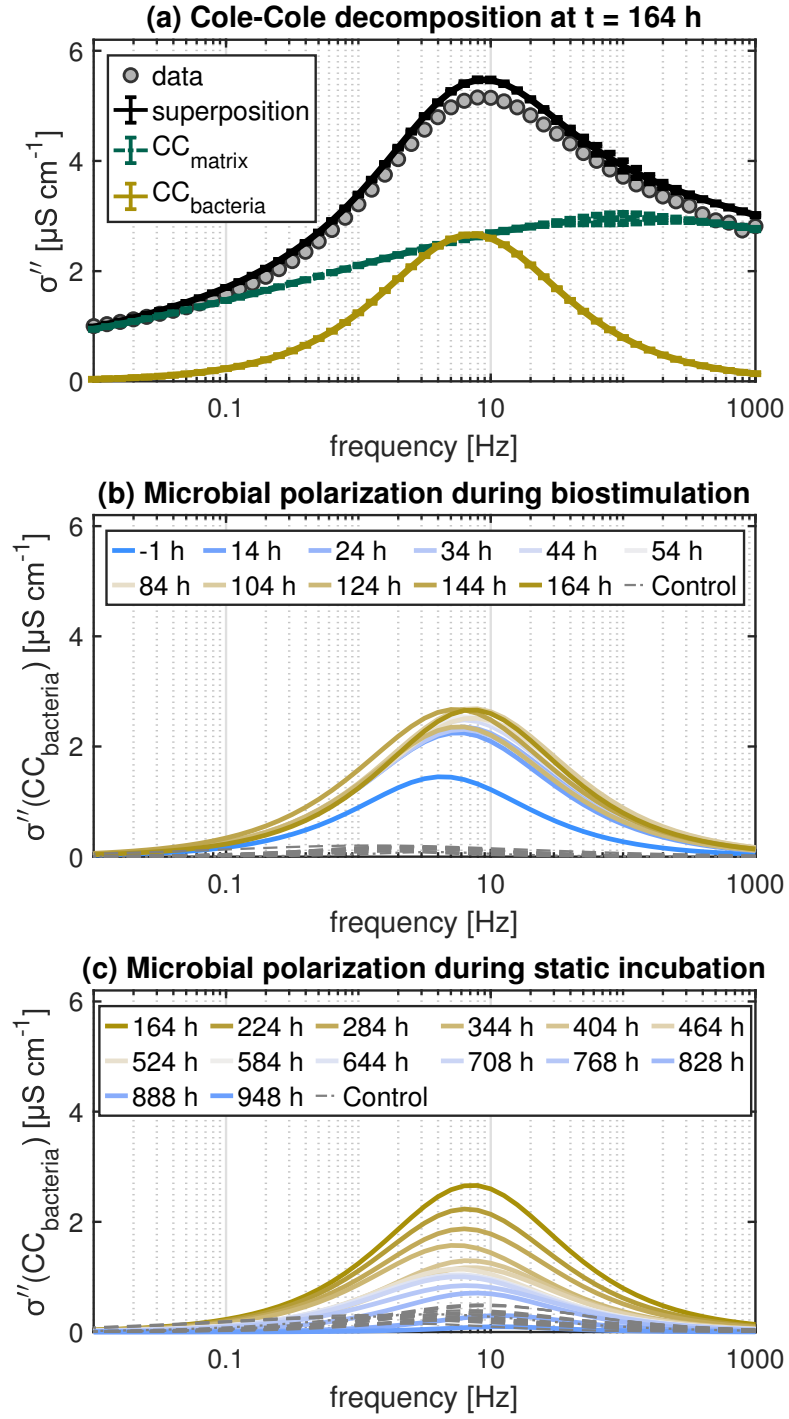


Figure 4.5: Cole-Cole decomposition of the spectrum at the end of the biostimulation phase, $t=164$ h, into its matrix and microbial component (a). Panels (b) and (c) show the microbial component to the overall polarization during biostimulation and static incubation, respectively. In grey, the results of the Cole-Cole decomposition applied to a control column that was not stimulated is shown.

5. Conclusions and outlook

Overall, the relative temporal dynamics of $\sigma''_{max} (CC_{bacteria})$ were similar to the measured σ''_{max} (figure 4.4c) confirming that σ'' changes were dominated by microbial activity during the denitrification experiment. The latter highlights that the polarization of cell surfaces can play a significant role in natural sediments despite their small volume fraction. The removal of the simultaneously changing matrix polarization provides access to the actual microbial polarization magnitudes, the relevant quantity for a future establishment of quantitative *organophysical* relationships between σ'' and microbial abundance and activity in different sediments or for different reactions.

5. Conclusions and outlook

In this thesis, I shed light on different aspects of reaction monitoring with SIP. In particular, I focused on methods to discriminate between different processes that contribute to σ'' signals in the context of reactions that involve organic matter or microbes in fully-saturated flow-through systems. I showed that OM significantly contributes to the background polarization of a mixed sediment even at a low TOC content. Additionally, I was successful at isolating the contribution of microbial processes from abiotic parallel processes contributing to σ'' signals. My experiments showed that SIP is sensitive enough to (1) detect reactions happening on the surface of OM and (2) changes in microbial activity in a natural sediment with background polarization. This is key to transfer the method towards application cases.

In section 4.2, I showed how $\Delta\sigma''$ vs. $\Delta\sigma'$ plots could be applied as diagnostic plots to qualitatively monitor solute breakthrough and cation exchange. Furthermore, I proposed a framework to quantitatively incorporate σ'' data into RTMs as a proxy for sorbed concentrations. In section 4.3 I then showed an easy-to-implement Cole-Cole decomposition approach that helped to discriminate between parallel polarization contributions. The Cole-Cole decomposition successfully differentiated between microbially active and microbially inactive zones and times, a very valuable qualitative

5. Conclusions and outlook

information for the monitoring of microbial reactions.

Requirements for a successful reaction monitoring In general, a successfully monitoring reactions with SIP requires a sufficient sensitivity of the method towards the reaction. This can be estimated beforehand by considering the background material, the type of reaction, and its effect on the EDL based on geochemical principles. Special care has to be taken to assess the effect of other geochemical parameters on the SIP signal that are altered in the course of the experiment. These include changes pH or electrical conductivity, precipitation/dissolution or sorption of reaction products. Often such parallel signal contributions are inherent to the experiment and cannot be prevented. On the contrary, if considered they can provide valuable information on the reactive system as well. In my thesis, I have presented different approaches to account for parallel signal contributions, either based on their different frequency-dependent polarization or in combination with a RTM. Applying these methods to other test cases and further refinement of them would strongly improve the applicability of SIP in reaction monitoring. Enhanced biostimulation projects (e.g. Critchley et al. [2014]) could benefit from SIP monitoring that would provide direct information on the success and spatial distribution of biostimulation. In particular, the *a priori* unknown duration of the "conditioning" or "lag" phase is directly observable by SIP without the need for sampling. Such online monitoring of microbial activity could open new options in terms of operational design and control of biostimulation projects. This is also the case for more controlled systems like biotechnology applications, where SIP is gaining increasing interest [Slouka et al. 2016; 2017; Turick et al. 2019].

SIP data processing and visualization for online monitoring During the different projects, visualization of multidimensional SIP data has been essential to draw conclusions from the acquired data. In this context, time series of the absolute change of σ'' and σ' at a single frequency in combination with a subset of spectra in the frequency domain have been proven particularly useful. Both can be processed without

5. Conclusions and outlook

prior knowledge from SIP data only and can thus help to understand reaction dynamics directly while the experiment is running. In previous studies, relative changes have often been used to visualize temporal changes in SIP data (e.g. Abdel Aal et al. [2010]; Mellage et al. [2019] or Rosier et al. [2019]) or single Cole-Cole fitted parameters have been shown over time (e.g. Mellage et al. [2019]). While this has the advantage of an easy comparison with other datasets, e.g. concentration time series, a large part of the information contained the signal is lost and noise can be exaggerated at locations where in absolute terms the signal is not changing significantly. Looking at the absolute change in contrast allows to compare different locations or experiments in their temporal evolution and signal magnitude. Choosing the frequency that is most sensitive to the reactive process can typically not be determined beforehand. A frequency in the range of 1 Hz - 10 Hz, where the SIP signal is less prone to measurement errors has been proven to be a good starting point. If the spectra then show strong frequency-dependent changes, this frequency might be updated at a later stage. For the identification of microbially-active zones, measurements over the entire frequency range (mHz to kHz) and a spectral decomposition using a double Cole-Cole model is suitable. Because the Cole-Cole decomposition presented in section 4.2 requires no site-specific geochemical data to constrain the parameters it has also the potential to serve as a diagnostic tool to identify microbially active zones already while an experiment is running. I decided not to present time series of Cole-Cole parameters but rather parameter-sets as fitted σ'' values, e.g. following the peak maximum of a Cole-Cole fit over time, because Cole-Cole parameters are strongly related[Bérubé et al. 2017; Fiandaca et al. 2018].

Limitations and potential research directions Besides sensitivity limitations, the effect of EC changes on σ'' poses a major challenge in interpreting $\Delta\sigma''$ changes. Whenever possible, experiments at which the EC is kept constant are advantageous to study specific processes. In laboratory experiments, equilibration of the sediments with the background solution until the EC at the outflow matches the inflow

5. Conclusions and outlook

EC strongly reduces the ambiguity in the observed signals. However, often it is impossible to keep the EC constant and a change in EC can also provide additional valuable information, e.g. on the breakthrough of the non-reactive solute front (as observable in $\Delta\sigma'$) compared to the reactive front (as observable by $\Delta\sigma''$). Further research is needed to elucidate the quantitative relationship between EC and σ'' in different sediments and complex multi-ionic pore water compositions, aiming for a correction procedure of the σ'' signal. In general, experiments under controlled conditions in which different polarization processes are induced at the same time will help to further refine separation workflows and to identify sensitivity limitations under specific conditions. Such experiments can also provide the basis to further advance the Cole-Cole decomposition, especially through a more rigorous (Bayesian) parameter estimation. By doing so, the quantitative potential of the decomposition approach could be investigated further. In addition, a more in-depth understanding of the polarization processes on cell surfaces is necessary for the monitoring of microbially-mediated reactions. In particular, understanding the effect of different metabolic states from dormant cells to actively growing cells greatly enhances the potential to incorporate σ'' data into RTM as a quantitative proxy for microbial abundance and activity.

Future work on different OM types and mixtures with other polarizing sediment components such as clay minerals could shed light on their relative importance under different environmental conditions. The experimental set-up used in section 4.1 was adopted from Mella et al. [2022b] and can be easily applied to other sediments or artificial mixtures, which would ensure the comparability across studies and the compilation of a larger database on *organo*-physical relationships. Furthermore, the complex conductivity signal of pure peats will require further investigation to better understand mechanisms determining the σ'' -signal in peatlands. An in-depth characterization of the geochemical conditions in peatlands, including the pH dependence of the CEC [Helling et al. 1964] will be necessary to understand the variability of the complex conductivity signal in purely organic environments.

6. References

Finally, technical advances are required to upscale the presented methods to field scale situations. Here, measurement errors due to inductive and capacitive coupling effects of the inevitable long cables limit the frequency-range strongly and correction methods are required to account for them (see e.g. Wang and Slater [2019]; Zhao et al. [2013]). In that context, it appears most promising to focus on actively induced reactions rather than trying to capture natural gradients in the presence of sediment heterogeneity. An intermediate step for upscaling could be monitoring of managed systems such as water filters for the removal of arsenic or nitrate (e.g. Li and Tabassum [2021]; Le et al. [2024]) with SIP, before approaching “real-world” conditions in the field.

6. References

- Abascal, E., Gómez-Coma, L., Ortiz, I., and Ortiz, A. (2022). Global diagnosis of nitrate pollution in groundwater and review of removal technologies. Science of The Total Environment, 810:152233.
- Abdel Aal, G. Z., Atekwana, E. A., Rossbach, S., and Werkema, D. D. (2010). Sensitivity of geoelectrical measurements to the presence of bacteria in porous media. Journal of Geophysical Research (1896-1977), 115(G3). Publisher: John Wiley & Sons, Ltd.
- Abdel Aal, G. Z., Atekwana, E. A., Slater, L. D., and Atekwana, E. A. (2004). Effects of microbial processes on electrolytic and interfacial electrical properties of unconsolidated sediments. Geophysical Research Letters, 31(12):n/a–n/a. Publisher: John Wiley & Sons, Ltd.
- Abdel Aal, G. Z., Slater, L. D., and Atekwana, E. A. (2006). Induced-polarization measurements on unconsolidated sediments from a site of active hydrocarbon biodegradation. Geophysics, 71(2):H13–H24. Publisher: Society of Exploration Geophysicists.

6. References

- Adamson, A. W. and Gast, A. P. (1997). Physical chemistry of surfaces. A Wiley-Interscience publication. Wiley, New York, 6. ed edition.
- Alberts, B. (2015). Molecular biology of the cell. Garland Science, Taylor and Francis Group, New York, NY, sixth edition edition.
- Amelung, W., Blume, H.-P., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K., and Wilke, B.-M. (2018). Scheffer/Schachtschabel Lehrbuch der Bodenkunde. Springer Berlin Heidelberg, Berlin, Heidelberg, 17., überarbeitete und ergänzte auflage edition.
- Barth, G. R., Hill, M. C., Illangasekare, T. H., and Rajaram, H. (2001). Predictive modeling of flow and transport in a two-dimensional intermediate-scale, heterogeneous porous medium. Water Resources Research, 37(10):2503–2512. Publisher: John Wiley & Sons, Ltd.
- Bate, B., Cao, J., Yang, Y., Cao, J., Zhang, C., and Zhang, S. (2023). Investigation of Cu Adsorption and Migration with Spectral Induced Polarization in Activated Carbon. Toxics, 11(3):221.
- Bücker, M., Flores Orozco, A., Undorf, S., and Kemna, A. (2019). On the Role of Stern- and Diffuse-Layer Polarization Mechanisms in Porous Media. Journal of Geophysical Research: Solid Earth, 124(6):5656–5677. Publisher: John Wiley & Sons, Ltd.
- Ben Moshe, S. and Furman, A. (2022). Real-time monitoring of organic contaminant adsorption in activated carbon filters using spectral induced polarization. Water Research, 212:118103.
- Ben Moshe, S., Kessouri, P., Erlich, D., and Furman, A. (2021). Geophysically based analysis of breakthrough curves and ion exchange processes in soil. Hydrology and Earth System Sciences, 25(6):3041–3052.

6. References

- Binley, A. and Slater, L. D. (2020). Resistivity and Induced Polarization. Cambridge University Press.
- Bérubé, C. L., Chouteau, M., Shamsipour, P., Enkin, R. J., and Olivo, G. R. (2017). Bayesian inference of spectral induced polarization parameters for laboratory complex resistivity measurements of rocks and soils. Computers & Geosciences, 105:51–64.
- Camargo, J. A. and Alonso, A. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environment International, 32(6):831–849.
- Carrol, D. (1959). Ion exchange in clays and other minerals. Geological Society of America Bulletin, 70(6):749.
- Cole, K. S. and Cole, R. H. (1941). Dispersion and Absorption in Dielectrics I. Alternating Current Characteristics. The Journal of Chemical Physics, 9(4):341–351. Publisher: American Institute of Physics.
- Comas, X. and Slater, L. (2004). Low-frequency electrical properties of peat. Water Resources Research, 40(12).
- Critchley, K., Rudolph, D. L., Devlin, J. F., and Schillig, P. C. (2014). Stimulating in situ denitrification in an aerobic, highly permeable municipal drinking water aquifer. Journal of Contaminant Hydrology, 171:66–80.
- Davis, C. A., Atekwana, E. A., Atekwana, E. A., Slater, L. D., Rossbach, S., and Mormile, M. R. (2006). Microbial growth and biofilm formation in geologic media is detected with complex conductivity measurements. Geophysical Research Letters, 33(18):n/a–n/a. Publisher: John Wiley & Sons, Ltd.
- Deng, Y., Shi, X., Zhang, Z., Sun, Y., Wu, J., and Qian, J. (2020). Application of spectral induced polarization for characterizing surfactant-enhanced DNAPL re-

6. References

- mediation in laboratory column experiments. Journal of Contaminant Hydrology, 230:103603.
- Fetter, C. W. (2008). Contaminant hydrogeology. Waveland Press, Long Grove, Ill, 2. ed., reissued edition.
- Fiandaca, G., Madsen, L. M., and Maurya, P. K. (2018). Re-parameterisations of the Cole–Cole model for improved spectral inversion of induced polarization data. Near Surface Geophysics, 16(4):385–399. Publisher: European Association of Geoscientists & Engineers.
- Flores Orozco, A., Gallistl, J., Steiner, M., Brandstätter, C., and Fellner, J. (2020). Mapping biogeochemically active zones in landfills with induced polarization imaging: The Heferlbach landfill. Waste Management, 107:121–132.
- Flores Orozco, A., Williams, K. H., Long, P. E., Hubbard, S. S., and Kemna, A. (2011). Using complex resistivity imaging to infer biogeochemical processes associated with bioremediation of an uranium-contaminated aquifer. Journal of Geophysical Research, 116(G3). Publisher: John Wiley & Sons, Ltd.
- Günther, T. and Martin, T. (2016). Spectral two-dimensional inversion of frequency-domain induced polarization data from a mining slag heap. Journal of Applied Geophysics, 135:436–448.
- Griebler, C. and Lueders, T. (2009). Microbial biodiversity in groundwater ecosystems. Freshwater Biology, 54(4):649–677. Publisher: John Wiley & Sons, Ltd.
- Groffman, P. M., Altabet, M. A., Böhlke, J. K., Butterbach-Bahl, K., David, M. B., Firestone, M. K., Giblin, A. E., Kana, T. M., Nielsen, L. P., and Voytek, M. A. (2006). METHODS FOR MEASURING DENITRIFICATION: DIVERSE APPROACHES TO A DIFFICULT PROBLEM. Ecological Applications, 16(6):2091–2122.
- Hao, N., Moysey, S. M. J., Powell, B. A., and Ntarlagiannis, D. (2015). Evaluation of Sur-

6. References

- face Sorption Processes Using Spectral Induced Polarization and a (22)Na Tracer. Environmental Science & Technology, 49(16):9866–9873.
- Hao, N., You, Y., Zhan, L.-T., and Bate, B. (2022). Evaluation of aqueous Cd²⁺ and Pb²⁺ removal by natural loess using spectral induced polarization and microscopic characterization. Environmental Science and Pollution Research, 29(33):50500–50514.
- Helling, C. S., Chesters, G., and Corey, R. B. (1964). Contribution of Organic Matter and Clay to Soil Cation-Exchange Capacity as Affected by the pH of the Saturating Solution. Soil Science Society of America Journal, 28(4):517–520.
- Himes, F. L. and Barber, S. A. (1957). Chelating Ability of Soil Organic Matter. Soil Science Society of America Journal, 21(4):368–373.
- Izumoto, S., Huisman, J. A., Zimmermann, E., Heyman, J., Gomez, F., Tabuteau, H., Laniel, R., Vereecken, H., Méheust, Y., and Le Borgne, T. (2022). Pore-Scale Mechanisms for Spectral Induced Polarization of Calcite Precipitation Inferred from Geo-Electrical Millifluidics. Environmental Science & Technology, 56(8):4998–5008. Publisher: American Chemical Society.
- Joo, H.-W., Kwon, T.-H., Lee, S.-R., and Wu, Y. (2021). Relaxation behavior in low-frequency complex conductivity of sands caused by bacterial growth and biofilm formation by *Shewanella oneidensis* under a high-salinity condition. Geophysics, 86(6):B389–B400.
- Jougnot, D., Ghorbani, A., Revil, A., Leroy, P., and Cosenza, P. (2010). Spectral induced polarization of partially saturated clay-rocks: a mechanistic approach. Geophysical Journal International, 180(1):210–224.
- Katona, T., Gilfedder, B. S., Frei, S., Bucker, M., and Flores Orozco, A. (2021). High-resolution induced polarization imaging of biogeochemical carbon-turnover hot spots in a peatland. Biogeosciences, 18(13):4039–4058.

6. References

- Kemna, A., Binley, A., Cassiani, G., Niederleithinger, E., Revil, A., Slater, L. D., Williams, K. H., Flores Orozco, A., Haegel, F.-H., Hördt, A., Kruschwitz, S., Leroux, V., Titov, K., and Zimmermann, E. (2012). An overview of the spectral induced polarization method for near-surface applications. Near Surface Geophysics, 10(6):453–468.
- Kessouri, P., Furman, A., Huisman, J. A., Martin, T., Mellage, A., Ntarlagiannis, D., Bücker, M., Ehosioke, S., Fernandez, P., Flores Orozco, A., Kemna, A., Nguyen, F., Pilawski, T., Saneiyan, S., Schmutz, M., Schwartz, N., Weigand, M., Wu, Y., Zhang, C., and Placencia-Gomez, E. (2019). Induced polarization applied to biogeophysics: recent advances and future prospects. Near Surface Geophysics, 17(6):595–621. Publisher: John Wiley & Sons, Ltd.
- Kimak, C., Ntarlagiannis, D., Slater, L. D., Atekwana, E. A., Beaver, C. L., Rossbach, S., Porter, A., and Ustra, A. (2019). Geophysical Monitoring of Hydrocarbon Biodegradation in Highly Conductive Environments. Journal of Geophysical Research: Biogeosciences, 124(2):353–366. Publisher: John Wiley & Sons, Ltd.
- Konings, W. N., Albers, S.-V., Koning, S., and Driessen, A. J. (2002). The cell membrane plays a crucial role in survival of bacteria and archaea in extreme environments. Antonie van Leeuwenhoek, 81(1-4):61–72.
- Koopal, L. K., van Riemsdijk, W. H., and Kinniburgh, D. G. (2001). Humic matter and contaminants. General aspects and modeling metal ion binding. Pure and Applied Chemistry, 73(12):2005–2016.
- Lanyi, J. K. (1979). The role of Na⁺ in transport processes of bacterial membranes. Biochimica et Biophysica Acta (BBA) - Reviews on Biomembranes, 559(4):377–397.
- Lapworth, D., Baran, N., Stuart, M., and Ward, R. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environmental Pollution, 163:287–303.
- Le, A. V., Muehe, E. M., Bone, S., Drabesch, S., Fischer, S., and Kappler, A. (2024).

6. References

- Field and Laboratory Evidence for Manganese Redox Cycling Controlling Iron and Arsenic Retention in Household Sand Filters. ACS ES&T Water, 4(1):33–43.
- Lennon, J. T. and Jones, S. E. (2011). Microbial seed banks: the ecological and evolutionary implications of dormancy. Nature Reviews Microbiology, 9(2):119–130. Publisher: Nature Publishing Group.
- Leroy, P. and Revil, A. (2009). A mechanistic model for the spectral induced polarization of clay materials. Journal of Geophysical Research, 114(B10). Publisher: John Wiley & Sons, Ltd.
- Leroy, P., Revil, A., Kemna, A., Cosenza, P., and Ghorbani, A. (2008). Complex conductivity of water-saturated packs of glass beads. Journal of Colloid and Interface Science, 321(1):103–117.
- Lesmes, D. P. and Morgan, F. D. (2001). Dielectric spectroscopy of sedimentary rocks. Journal of Geophysical Research, 106(B7):13329–13346. Publisher: John Wiley & Sons, Ltd.
- Li, J. and Tabassum, S. (2021). Remediation of nitrate-contaminated groundwater by a combined treatment method of novel Mass Bio System and solid organic carbon sources: In-depth study. Cleaner Engineering and Technology, 4:100161.
- Li, L., Maher, K., Navarre-Sitchler, A., Druhan, J., Meile, C., Lawrence, C., Moore, J., Perdrial, J., Sullivan, P. L., Thompson, A., Jin, L., Bolton, E. W., Brantley, S. L., Dietrich, W. E., Mayer, K. U., Steefel, C. I., Valocchi, A., Zachara, J., Kocar, B., McIntosh, J., Tutolo, B. M., Kumar, M., Sonnenthal, E., Bao, C., and Beisman, J. (2017). Expanding the role of reactive transport models in critical zone processes. Earth-Science Reviews, 165:280–301.
- Li, L., Sullivan, P. L., Benettin, P., Cirpka, O. A., Bishop, K., Brantley, S. L., Knapp, J. L. A., Meerveld, I., Rinaldo, A., Seibert, J., Wen, H., and Kirchner, J. W. (2021). Toward catchment hydro-biogeochemical theories. WIREs Water, 8(1):e1495. Publisher: John Wiley & Sons, Ltd.

6. References

- Maloney, P. C., Kashket, E. R., and Wilson, T. H. (1974). A protonmotive force drives ATP synthesis in bacteria. Proceedings of the National Academy of Sciences of the United States of America, 71(10):3896–3900.
- Marshall, D. J. and Madden, T. R. (1959). Induced polarization, a study of its causes. Geophysics, 24(4):790–816. Publisher: Society of Exploration Geophysicists.
- Mellage, A., Dörrich, M., and Haderlein, S. B. (2022a). Capturing In Situ Glyphosate (De)sorption Kinetics in Floodplain Aquifer Sediment Columns: Geophysical Measurements and Reactive Transport Modeling. Environmental Science & Technology.
- Mellage, A., Eckert, D., Grösbacher, M., Inan, A. Z., Cirpka, O. A., and Griebler, C. (2015). Dynamics of suspended and attached aerobic toluene degraders in small-scale flow-through sediment systems under growth and starvation conditions. Environmental Science & Technology, 49(12):7161–7169. Publisher: American Chemical Society.
- Mellage, A., Smeaton, C. M., Furman, A., Atekwana, E. A., Rezanezhad, F., and Van Cappellen, P. (2018). Linking Spectral Induced Polarization (SIP) and Subsurface Microbial Processes: Results from Sand Column Incubation Experiments. Environmental Science & Technology, 52(4):2081–2090. Publisher: American Chemical Society.
- Mellage, A., Smeaton, C. M., Furman, A., Atekwana, E. A., Rezanezhad, F., and Van Cappellen, P. (2019). Bacterial Stern layer diffusion: experimental determination with spectral induced polarization and sensitivity to nitrite toxicity. Near Surface Geophysics, 17(6):623–635.
- Mellage, A., Zakai, G., Efrati, B., Pagel, H., and Schwartz, N. (2022b). Paraquat sorption- and organic matter-induced modifications of soil spectral induced polarization (SIP) signals. Geophysical Journal International, 229(2):1422–1433.
- Ntarlagiannis, D., Doherty, R., and Williams, K. H. (2010). Spectral induced polarization signatures of abiotic FeS precipitation. Geophysics, 75(4):F127–F133.

6. References

- Ntarlagiannis, D., Williams, K. H., Slater, L. D., and Hubbard, S. S. (2005). Low-frequency electrical response to microbial induced sulfide precipitation. Journal of Geophysical Research, 110(G2):n/a–n/a. Publisher: John Wiley & Sons, Ltd.
- Obiri-Nyarko, F., Grajales-Mesa, S. J., and Malina, G. (2014). An overview of permeable reactive barriers for in situ sustainable groundwater remediation. Chemosphere, 111:243–259.
- Pelton, W. H., Ward, S. H., Hallof, P. G., Sill, W. R., and Nelson, P. H. (1978). Mineral discrimination and removal of inductive coupling with multifrequency IP. Geophysics, 43(3):588–609. Publisher: Society of Exploration Geophysicists.
- Pinay, G., Peiffer, S., Dreuz, J.-R., Krause, S., Hannah, D. M., Fleckenstein, J. H., Sebbelo, M., Bishop, K., and Hubert-Moy, L. (2015). Upscaling Nitrogen Removal Capacity from Local Hotspots to Low Stream Orders' Drainage Basins. Ecosystems, 18(6):1101–1120.
- Placencia-Gomez, E., Robinson, J., Slater, L., and Qafoku, N. P. (2022). Spectral induced polarization monitoring of induced calcite precipitation in subsurface sediments. Geophysical Journal International.
- Podgorski, J. and Berg, M. (2020). Global threat of arsenic in groundwater. Science, 368(6493):845–850.
- Ponziani, M., Slob, E. C., Vanhala, H., and Ngan-Tillard, D. (2012). Influence of physical and chemical properties on the low-frequency complex conductivity of peat. Near Surface Geophysics, 10(6):491–501.
- Poortinga, A. T., Bos, R., Norde, W., and Busscher, H. J. (2002). Electric double layer interactions in bacterial adhesion to surfaces. Surface Science Reports, 47(1):1–32.
- Rahmani, A., Franz, M., Bär, F., Backes, C., Byrne, J. M., and Mellage, A. (2024). Chang-

6. References

- ing Cr-Retention Capacity of Magnetite-Coated Sand Captured by Spectral Induced Polarization (SIP). ACS ES&T Water, page acsestwater.3c00824.
- Randhawa, N. S. and Broadbent, F. E. (1965). SOIL ORGANIC MATTER-METAL COMPLEXES: 5. REACTIONS OF ZINC WITH MODEL COMPOUNDS AND HUMIC ACID. Soil Science, 99(5).
- Revil, A. (2012). Spectral induced polarization of shaly sands: Influence of the electrical double layer. Water Resources Research, 48(2).
- Revil, A., Atekwana, E. A., Zhang, C., Jardani, A., and Smith, S. (2012a). A new model for the spectral induced polarization signature of bacterial growth in porous media. Water Resources Research, 48(9). Publisher: John Wiley & Sons, Ltd.
- Revil, A., Ghorbani, A., Jougnot, D., and Yven, B. (2023). Induced polarization of clay-rich materials — Part 1: The effect of desiccation. Geophysics, pages 1–57.
- Revil, A., Karaoulis, M., Johnson, T., and Kemna, A. (2012b). Review: Some low-frequency electrical methods for subsurface characterization and monitoring in hydrogeology. Hydrogeology Journal, 20(4):617–658.
- Revil, A. and Skold, M. (2011). Salinity dependence of spectral induced polarization in sands and sandstones. Geophysical Journal International, 187(2):813–824.
- Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W., and Bemment, C. D. (2008a). Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. Water Research, 42(16):4215–4232.
- Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W. N., and Bemment, C. D. (2008b). Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Research, 42(16):4215–4232.
- Rosier, C. L., Atekwana, E. A., Abdel Aal, G. Z., and Patrauchan, M. A. (2019). Cell concentrations and metabolites enhance the SIP response to biofilm matrix components. Journal of Applied Geophysics, 160:183–194.

6. References

- Rubin, Y., Hubbard, S. S., and Singh, V. P., editors (2005). Hydrogeophysics, volume 50 of Water Science and Technology Library. Springer Netherlands, Dordrecht.
- Saneiyan, S. (2019). Geophysical methods for monitoring soil stabilization by microbial induced carbonate precipitation. Doctoral thesis, Rutgers University, Newark, U.S.
- Saneiyan, S., Ntarlagiannis, D., and Colwell, F. (2020). Complex conductivity signatures of microbial induced calcite precipitation, field and laboratory scales. Geophysical Journal International, 224(3):1811–1824.
- Schwartz, N. and Furman, A. (2014). On the spectral induced polarization signature of soil organic matter. Geophysical Journal International, 200(1):589–595.
- Schwarz, G. (1962). A THEORY OF THE LOW-FREQUENCY DIELECTRIC DISPERSION OF COLLOIDAL PARTICLES IN ELECTROLYTE SOLUTION 1,2. The Journal of Physical Chemistry, 66(12):2636–2642.
- Scott, J. and Barker, R. D. (2003). Determining pore-throat size in Permo-Triassic sandstones from low-frequency electrical spectroscopy. Geophysical Research Letters, 30(9).
- Scow, K. M. and Hicks, K. A. (2005). Natural attenuation and enhanced bioremediation of organic contaminants in groundwater. Current Opinion in Biotechnology, 16(3):246–253.
- Slater, L. D. and Glaser, D. R. (2003). Controls on induced polarization in sandy unconsolidated sediments and application to aquifer characterization. Geophysics, 68(5):1547–1558.
- Slouka, C., Brunauer, G., Kopp, J., Strahammer, M., Fricke, J., Fleig, J., and Herwig, C. (2017). Low-Frequency Electrochemical Impedance Spectroscopy as a Monitoring Tool for Yeast Growth in Industrial Brewing Processes. Chemosensors, 5(3):24.

6. References

- Slouka, C., Wurm, D. J., Brunauer, G., Welzl-Wachter, A., Spadiut, O., Fleig, J., and Herwig, C. (2016). A Novel Application for Low Frequency Electrochemical Impedance Spectroscopy as an Online Process Monitoring Tool for Viable Cell Concentrations. Sensors (Basel, Switzerland), 16(11).
- Smith, M., Cross, K., Paden, M., and Laban, P., editors (2016). Spring : managing groundwater sustainably. International Union for Conservation of Nature and Natural Resources.
- Stolpovsky, K., Martinez-Lavanchy, P., Heipieper, H. J., Van Cappellen, P., and Thullner, M. (2011). Incorporating dormancy in dynamic microbial community models. Ecological Modelling, 222(17):3092–3102.
- Strobel, C., Abramov, S., Huisman, J. A., Cirpka, O. A., and Melage, A. (2023a). Spectral Induced Polarization (SIP) of Denitrification-Driven Microbial Activity in Column Experiments Packed With Calcareous Aquifer Sediments. Journal of Geophysical Research: Biogeosciences, 128(1).
- Strobel, C., Doerrich, M., Stieff, E., Huisman, J. A., Cirpka, O. A., and Melage, A. (2023b). Organic Matter Matters—The Imaginary Conductivity of Sediments Rich in Solid Organic Carbon. Geophysical Research Letters, 50(23):e2023GL104630.
- Strobel, C., Störiko, A., Cirpka, O. A., and Melage, A. (2024). Are we there yet? A critical experimental assessment of the application of induced polarization for monitoring geochemical processes. Geochimica et Cosmochimica Acta.
- Suarez, M. P. and Rifai, H. S. (1999). Biodegradation Rates for Fuel Hydrocarbons and Chlorinated Solvents in Groundwater. Bioremediation Journal, 3(4):337–362.
- Titov, K., Komarov, V., Tarasov, V., and Levitski, A. (2002). Theoretical and experimental study of time domain-induced polarization in water-saturated sands. Journal of Applied Geophysics, 50(4):417–433.

6. References

- Turick, C. E., Shimpalee, S., Satjaritanun, P., Weidner, J., and Greenway, S. (2019). Convenient non-invasive electrochemical techniques to monitor microbial processes: current state and perspectives. Applied Microbiology and Biotechnology, 103(20):8327–8338.
- van der Wal, A., Minor, Norde, Zehnder, and Lyklema (1997). Conductivity and Dielectric Dispersion of Gram-Positive Bacterial Cells. Journal of Colloid and Interface Science, 186(1):71–79.
- Vaudelet, P., Revil, A., Schmutz, M., Franceschi, M., and Bégassat, P. (2011). Induced polarization signatures of cations exhibiting differential sorption behaviors in saturated sands. Water Resources Research, 47(2). Publisher: John Wiley & Sons, Ltd.
- Wang, C. and Slater, L. D. (2019). Extending accurate spectral induced polarization measurements into the kHz range: modelling and removal of errors from interactions between the parasitic capacitive coupling and the sample holder. Geophysical Journal International, 218(2):895–912.
- Weigand, M. and Kemna, A. (2016). Debye decomposition of time-lapse spectral induced polarisation data. Computers & Geosciences, 86:34–45.
- Weller, A., Breede, K., Slater, L., and Nordsiek, S. (2011). Effect of changing water salinity on complex conductivity spectra of sandstones. GEOPHYSICS, 76(5):F315–F327.
- Weller, A. and Slater, L. (2012). Salinity dependence of complex conductivity of unconsolidated and consolidated materials: Comparisons with electrical double layer models. Geophysics, 77(5):D185–D198.
- Weller, A. and Slater, L. D. (2019). Permeability estimation from induced polarization: an evaluation of geophysical length scales using an effective hydraulic radius concept. Near Surface Geophysics, 17(6):581–594.

6. References

- Werth, C. J., Zhang, C., Brusseau, M. L., Oostrom, M., and Baumann, T. (2010). A review of non-invasive imaging methods and applications in contaminant hydrogeology research. Journal of Contaminant Hydrology, 113(1-4):1–24.
- Wick, K., Heumesser, C., and Schmid, E. (2012). Groundwater nitrate contamination: Factors and indicators. Journal of Environmental Management, 111:178–186.
- Williams, K. H., Kemna, A., Wilkins, M. J., Druhan, J., Arntzen, E., N’Guessan, A. L., Long, P. E., Hubbard, S. S., and Banfield, J. F. (2009). Geophysical monitoring of coupled microbial and geochemical processes during stimulated subsurface bioremediation. Environmental Science & Technology, 43(17):6717–6723. Publisher: American Chemical Society.
- Zhang, C., Revil, A., Fujita, Y., Munakata-Marr, J., and Redden, G. (2014). Quadrature conductivity: A quantitative indicator of bacterial abundance in porous media. Geophysics, 79(6):D363–D375.
- Zhao, Y., Zimmermann, E., Huisman, J. A., Treichel, A., Wolters, B., van Waasen, S., and Kemna, A. (2013). Broadband EIT borehole measurements with high phase accuracy using numerical corrections of electromagnetic coupling effects. Measurement Science and Technology, 24(8):085005. Publisher: IOP Publishing.

A. Appendix

A.1. Publication 1

JGR Biogeosciences

RESEARCH ARTICLE

10.1029/2022JG007190

Key Points:

- Microbial denitrification in natural sediments can be tracked using spectral induced polarization (SIP)
- σ'' spectra of a natural microbial community match reported spectra from single strains and the level of microbial activity affects σ''
- Superimposing Cole-Cole terms provides a framework for separating microbial and abiotic contributions from SIP signals

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

C. Strobel and A. Mellaé,
cora.strobel@uni-tuebingen.de;
adrian.mellaé@uni-kassel.de

Citation:

Strobel, C., Abramov, S., Huisman, J. A., Cirpka, O. A., & Mellaé, A. (2023). Spectral induced polarization (SIP) of denitrification-driven microbial activity in column experiments packed with calcareous aquifer sediments. *Journal of Geophysical Research: Biogeosciences*, 128, e2022JG007190. <https://doi.org/10.1029/2022JG007190>

Received 16 SEP 2022

Accepted 28 DEC 2022

Author Contributions:

Conceptualization: C. Strobel, J. A.

Huisman, O. A., Cirpka, A. Mellaé

Formal analysis: C. Strobel

Funding acquisition: A. Mellaé

Investigation: C. Strobel, S. Abramov

Methodology: C. Strobel, S. Abramov, A. Mellaé

Project Administration: A. Mellaé

Resources: O. A. Cirpka

Software: C. Strobel, A. Mellaé

Supervision: J. A. Huisman, O. A.

Cirpka, A. Mellaé

© 2023 The Authors.

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial License](#), which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Spectral Induced Polarization (SIP) of Denitrification-Driven Microbial Activity in Column Experiments Packed With Calcareous Aquifer Sediments

C. Strobel^{1,2} , S. Abramov^{1,3}, J. A. Huisman⁴ , O. A. Cirpka¹ , and A. Mellaé² 

¹Department of Geosciences, University of Tübingen, Tübingen, Germany, ²Civil and Environmental Engineering, University of Kassel, Kassel, Germany, ³Department of Environmental Microbiology, Institute of Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart, Stuttgart, Germany, ⁴Agrosphere (IBG-3), Institute of Bio- and Geosciences, Forschungszentrum Jülich GmbH, Jülich, Germany

Abstract Spectral Induced Polarization (SIP) has been suggested as a non-invasive monitoring proxy for microbial processes. Under natural conditions, however, multiple and often coupled polarization processes co-occur, impeding the interpretation of SIP signals. In this study, we analyze the sensitivity of SIP to microbially-driven reactions under quasi-natural conditions. We conducted flow-through experiments in columns equipped with SIP electrodes and filled with natural calcareous, organic-carbon-rich aquifer sediment, in which heterotrophic denitrification was bio-stimulated. Our results show that, even in the presence of parallel polarization processes in a natural sediment under field-relevant geochemical conditions, SIP is sufficiently sensitive to microbially-driven changes in electrical charge storage. Denitrification yielded an increase in imaginary conductivity of up to $3.1 \mu\text{S cm}^{-1}$ (+140%) and the formation of a distinct peak between 1 and 10 Hz, that matched the timing of expected microbial activity predicted by a reactive transport model fitted to solute concentrations. A Cole-Cole decomposition allowed separating the polarization contribution of microbial activity from that of cation exchange, thereby helping to locate microbial hotspots without the need for (bio) geochemical data to constrain the Cole-Cole parameters. Our approach opens new avenues for the application of SIP as a rapid method to monitor a system's reactivity in situ. While in preceding studies the SIP signals of microbial activity in natural sediments were influenced by mineral precipitation/dissolution reactions, the imaginary conductivity changes measured in the biostimulation experiments presented here were dominated by changes in the polarization of the bacterial cells rather than a reaction-induced alteration of the abiotic matrix.

Plain Language Summary To better predict the contribution of microbes to groundwater clean-up it is important to locate microbes in the ground that are actively removing contaminants and measure how fast they are doing so. Our ability to do so, however, is limited by the difficulty in visualizing underground processes. Electrical methods such as spectral induced polarization (SIP) have been applied to monitor microbes and provide an alternative to visualize them underground. SIP, however, has so far only been shown to work in controlled environments and its sensitivity in natural systems remains a question. In this study, we conducted experiments with sediment collected from an underground aquifer, in which we stimulated microbial activity through the addition of nitrate, a widespread groundwater contaminant. Our results show that microbial consumption of nitrate causes a distinct SIP signal that is similar to SIP signals of bacteria in previously studied well-controlled systems. Furthermore, we propose an approach to separate the SIP signal of microbes from that of other processes that occur in natural groundwater. This enables us to quickly assess where the microbes are active and can potentially improve future experiments through the localization of microbial hot-spots and SIP-guided sampling for more detailed microbiological analysis.

1. Introduction

Microbially mediated reactions facilitate the in situ degradation of many contaminants in groundwater thus contributing substantially to the water-purification capabilities of the subsurface (Griebler & Avramov, 2015). The ability to understand and predict contaminant removal through microbially mediated reactions in aquifers hinges on our ability to monitor and quantify reaction rates (Pinay et al., 2015) and microbial activity in the subsurface (Leckie et al., 2004). Microbially mediated reactions are subject to spatial variability and temporal dynamics (Li et al., 2021). In general, that spatial variability depends on the co-occurrence of reactants and

Visualization: C. Strobel
Writing – original draft: C. Strobel
Writing – review & editing: C. Strobel,
S. Abramov, J. A. Huisman, O. A. Cirpka,
A. Mellage

microorganisms, the physicochemical conditions (e.g., temperature and pH), a sufficiently long contact time, and the absence of inhibitors or biotoxins. Direct, non-destructive observations of these parameters over different scales are not possible. Instead, information must be inferred from expensive point measurements, for example, breakthrough curves of solute concentrations at single observation points, or destructive methods (drillings, core extraction), both in field surveys and in laboratory experiments (Werth et al., 2010). Traditional methods for the quantification of microbial abundance, activity and community composition have to rely on destructively-sampled sediment because 80% to >99.9% of the bacteria in groundwater are located at the surfaces of the solid matrix rather than in the mobile water phase (Griebler & Lueders, 2009; Mellage et al., 2015). This is a severe limitation in bench-scale experiments in which sacrificial sampling based on preliminary knowledge can, but not necessarily will capture reaction dynamics (Störko et al., 2022). Thus, finding easy-to-measure proxies for microbial activity is key for improved monitoring of microbially mediated reactions in porous media.

The reaction of interest of this study is denitrification, that is, the microbial reduction of nitrate (NO_3^-) via several intermediates to N_2 , typically coupled to the oxidation of organic carbon, or inorganic electron donors such as Fe(II) or reduced sulfur compounds (Rivett et al., 2008). Excess nitrate, mostly stemming from agriculture, is ubiquitous in aquifers worldwide (Abascal et al., 2022). In oxic environments, NO_3^- is persistent and poses a potential risk to human health when present in sufficiently high concentrations ($>10 \text{ mg NO}_3^- \text{-N L}^{-1}$) in drinking water (Camargo & Alonso, 2006). Denitrification requires the presence of a suitable electron donor, denitrifying bacteria, the absence of oxygen (Kuypers et al., 2018), and sufficiently low flow velocities (Oldham et al., 2013). We chose denitrification and its associated microbial activity, in part, due to their environmental relevance and the challenges that are associated with the quantification of denitrification rates and their monitoring in the field.

Direct measurements of in situ denitrification rates are not only difficult and time consuming (Pinay et al., 2015), their relevance at the larger aquifer-scale is limited by the high spatio-temporal variability of reactive transport in aquifers (Groffman et al., 2006). Gierczak et al. (2007) and Critchley et al. (2014) demonstrated the strong dependence of stimulated in situ denitrification at field sites on the local flow conditions and the microbial response to the addition of an electron donor. Critchley et al. (2014) observed a conditioning phase in which the electron donor, acetate, was injected without any visible effect on NO_3^- -concentrations. The conditioning phase was of variable duration at different depths and at different monitoring wells, demonstrating the need to monitor the microbial response in real time and at high spatial resolution.

Non-invasive (bio)geophysical methods offer a promising monitoring alternative that can provide high-resolution information necessary to locate reactive zones in situ and capture reaction dynamics over time (Atekwana & Slater, 2009). Spectral induced polarization (SIP), in particular, has been shown to be sensitive to reactive transport processes, the abundance of bacteria and their metabolic activity in groundwater (see Atekwana & Slater, 2009; Kessouri et al., 2019 for a review). Among the other geophysical methods that have been used for reaction monitoring are seismics and direct-current (DC) geoelectrics (Che-Alota et al., 2009; Williams et al., 2005). The latter methods, however, do not depend on microbial activity itself but on its impact on the physical properties of the matrix or pore fluid, for example, mineral precipitation-driven changes in sediment stiffness (e.g., Saneiyani et al., 2020). Thus, limiting the applicability and transferability of such methods to other sites or reaction types. Conversely, the measurement principle of SIP is directly sensitive to the electrochemical properties of microbes (Kessouri et al., 2019) and could, in theory, be applied to any microbially-mediated reaction system.

In SIP, an alternating current at different frequencies in the mHz to kHz range is injected into the subsurface via an electrode pair, and the voltage is measured by a second pair (Marshall & Madden, 1959). The resulting impedance Z (Ω) and phase shift $-\Phi$ (rad) are typically expressed in the complex-valued phase notation. The corresponding material property, the conductivity σ^* (S m^{-1}), is also complex-valued. Its magnitude depends on electrical conduction through the pore fluid and along charged surfaces as well as on reversible electrical storage at charged surfaces (e.g., Binley & Slater, 2020 and references therein). In the applied frequency range, the real (in-phase) component σ' (S m^{-1}) is hardly affected by the small phase shifts in the mrad-range. It is almost identical to the DC conductivity, σ_0 (S m^{-1}), and mainly depends on the electrical conductance, σ_{el} (S m^{-1}), of the pore fluid through connected pores and, to a smaller extent, on electrical conduction along the grain-fluid interface, σ_{surf} (Slater & Glaser, 2003). The imaginary (out-of-phase or quadrature) conductivity, σ'' (S m^{-1}), is much smaller than σ' . It is approximately proportional to the product of the phase shift Φ and the DC conductivity and exhibits a strong frequency-dependence. Phenomenological models, such as the Cole-Cole relaxation model (Cole & Cole, 1941; Pelton et al., 1978), are commonly employed to help summarize the frequency dependent

polarization behavior of SIP measurements via a few characteristic parameters. Such models can be particularly helpful to analyze spectral data sets over time as they enable the quantification of changes in spectral shape and peak frequency alongside changes in the magnitude of polarization (Mellage, Smeaton, et al., 2018; Ntarlagiannis et al., 2010).

In porous media, in the absence of metallic particles and in the low-frequency range (mHz to kHz), charge storage is mainly controlled by electrochemical polarization of the electrical double layer (EDL) that surrounds the charged surfaces of minerals and colloids. Both the polarization of the EDL of single particles, mainly in the Stern layer (Leroy et al., 2008; Lesmes & Morgan, 2001; Schwarz, 1962) and membrane polarization, caused by a difference in the mobility of anions and cations at pore throats, contribute to charge storage (Marshall & Madden, 1959; Revil & Florsch, 2010; Titov et al., 2002). Several modeling approaches have been successful at predicting the spectral responses of glass beads and clay minerals by accounting for Stern layer polarization only (e.g., Jougnot et al., 2010; Leroy & Revil, 2009; Leroy et al., 2008). The properties of the EDL directly influence the magnitude and spectral dependency of σ'' responses. A higher surface charge leads to a higher concentration of counter ions within the EDL, yielding higher σ'' signals (Hao et al., 2015). The peak frequency is dependent on the length scale of polarization, that is, the particle size or pore size (e.g., Scott & Barker, 2003; Titov et al., 2002; Weller & Slater, 2019), and the mobility of the counter ions in the EDL (Schwarz, 1962). In porous media saturated with solutions containing more than two ions, the replacement of monovalent cations by divalent cations is known to reduce the magnitude of charge storage, due to their difference in surface mobility (Ben Moshe et al., 2021). Consequently, σ'' depends on both the ionic composition of the pore fluid and the surface properties of the matrix.

The polarization of microbes is to some extent similar to electrochemical polarization on mineral surfaces. Their cell-membrane surface contains charged functional groups that yield a net-negatively charged surface in the near neutral pH range (Poortinga et al., 2002). Moreover, the cell membrane acts as an electrical insulator between the cell interior and bulk solution (van der Wal et al., 1997). Thus, microbes can be conceptualized as additional particles that contribute to the overall complex-conductivity response of a porous medium (Kessouri et al., 2019; Mellage et al., 2019; Revil et al., 2012; Sanchis et al., 2007).

In biogeophysical studies, σ'' responses have been linked to microbial abundance and growth, not only in cell suspensions (Rosier et al., 2019; Zhang et al., 2014), but also in porous matrices that exhibit a low background polarization, such as glass beads and quartz sand (Abdel Aal et al., 2010; Davis et al., 2006; Mellage, Smeaton, et al., 2018). SIP has been successfully used to study nitrate reduction in sands (Mellage, Holmes, et al., 2018; Mellage et al., 2019), hydrocarbon degradation (Abdel Aal et al., 2004, 2006; Kimak et al., 2019), bacterial growth in a saline environment (Joo et al., 2021) and microbially induced precipitation of calcite (Saneiyani et al., 2019) and sulfide (Ntarlagiannis et al., 2005; Williams et al., 2005) at the laboratory scale, highlighting the potential of SIP to serve as a monitoring tool for a variety of microbially mediated processes. The method has also gained increasing interest in the live-monitoring of bioreactors (Turick et al., 2019). Electrical impedance spectroscopy (EIS), a 2-point measurement technique similar to SIP, is used by bioelectrochemists, where “low-frequency EIS” refers to the same frequency range that is traditionally used in biogeophysics. Slouka et al. (2016) refer to their 4-point measurements of microbial growth also as low frequency EIS but the measurement set-up is very similar to SIP measurements. Reported peak frequencies or fitted Cole-Cole peak frequencies that are related to the presence of bacteria range from 0.1 to 1 Hz (Joo et al., 2021; Zhang et al., 2014) to 2–30 Hz (Mellage, Holmes, et al., 2018; Mellage et al., 2019; Rosier et al., 2019; Zhang et al., 2014). In other studies, spectra were not presented or not acquired. Instead, complex conductivity was monitored at a specific frequency, typically 1 Hz (Katona et al., 2021) or 10 Hz (Abdel Aal et al., 2010).

Despite growing evidence that SIP signals are affected by microbial abundance and activity, the unique attribution of SIP signals to microbial processes in natural sediments has not been investigated and might be more difficult to capture than in packings of glass beads or clean quartz sand. Hence, we see the need for experiments of increased complexity, yet under controlled laboratory conditions, to investigate the sensitivity of SIP toward microbial reactions and to develop quantitative relationships between microbial abundance or activity and σ'' in the presence of other processes that contribute to SIP signals. The aim of the present study is to answer the following questions: (a) Do microbial reactions yield a measurable SIP signal under close-to-natural conditions? (b) What is the σ'' spectrum of a natural microbial community? and (c) What information is required to separate the microbial σ'' signals from parallel abiotic polarization processes? To this end, we stimulated microbial denitrification in an organic-carbon-rich calcareous sediment with its indigenous microbial community by injecting nitrate into

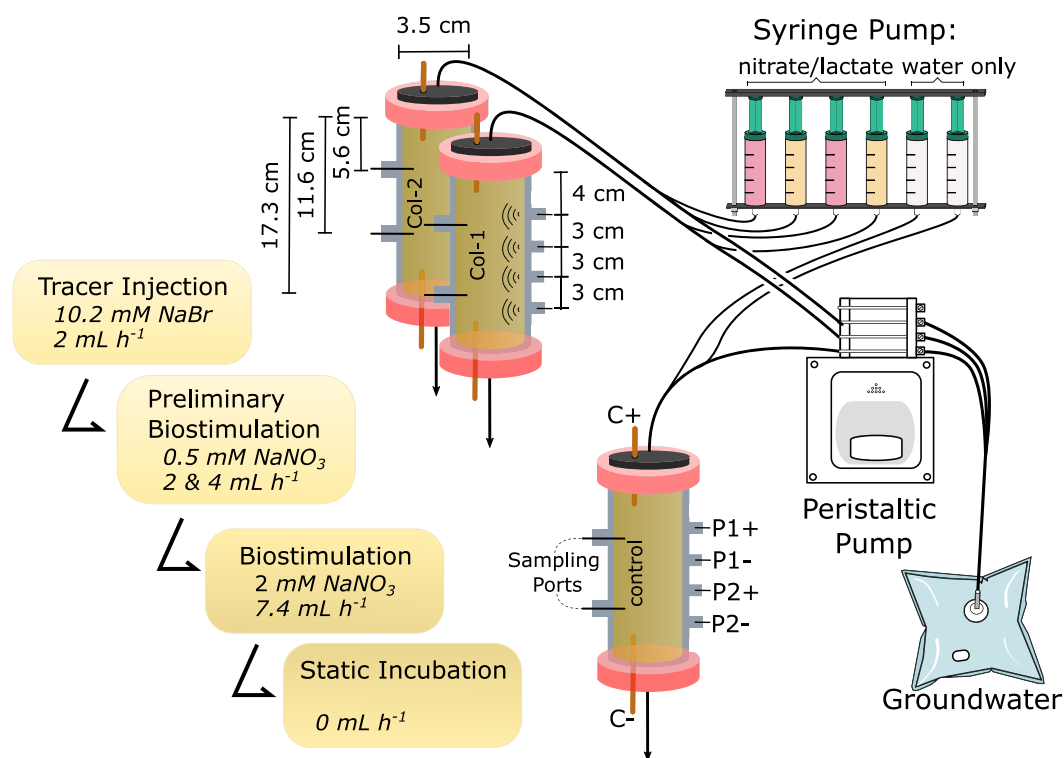


Figure 1. Experimental setup: The columns were equipped with four potential electrodes along the flow path and two current electrodes at the top and bottom caps. Two pore water sampling ports were located at 5.6 and 11.6 cm from the inlet. The inflowing solution consisted of natural anoxic groundwater, to which the tracer salts were added directly before the inlet using a syringe pump.

flow-through columns. Therein, we obtained breakthrough curves of reactants and synchronously measured changes in the σ'' spectrum. We jointly interpret these data to link the dynamic, denitrification-driven activity of the natural microbial community to the measured σ'' signals. To separate the effects of microbial activity and abiotic ion-exchange reactions we also performed experiments in which we injected a NaBr pulse. We propose a Cole-Cole decomposition (using two terms) in which one set of parameters relates to the abiotic contribution of the bulk polarization response, and the other set of parameters to the microbial contribution. Furthermore, we fitted a reactive transport model to the concentration time series of both the NaBr- and NO_3^- -injection phases to quantitatively relate SIP signals to ion exchange reactions and denitrifying microbial activity.

2. Materials and Methods

2.1. Setup of Flow-Through Columns

The flow-through experiment was conducted in four phases of different inflow conditions in three columns, out of which two served as biostimulated duplicates, Col-1 and Col-2, and one served as the non-biostimulated control. Figure 1 shows the experimental flow-through set-up with three glass columns ($L = 17.3$ cm, $d = 3.5$ cm) and an inflow system made up of a peristaltic pump that provided groundwater and a syringe pump for the addition of reactants, that is, sodium bromide (NaBr), sodium nitrate (NaNO_3) or sodium lactate (NaLac). The ratio of groundwater to reactant-containing solution was 10:1 (v/v). Each column was fitted with brass electrodes ($d = 0.5$ cm) at the column inlet and outlet for current injection, and four brass potential electrodes ($d = 0.5$ cm) 4, 7, 10, and 13 cm from the inlet. The potential electrodes were retracted from the current flow path and encased in an agar gel electrolyte. Additionally, each column was equipped with ceramic samplers at 5.6 and 11.6 cm from the inlet that facilitated the sampling of pore water at the midpoint of the potential electrode pairs. The columns were wet packed at ambient air with homogenized sediment from a depth of 2.4–7.4 m of the Ammer flood-plain aquifer, near Tübingen, Germany, henceforth referred to as the Tufa aquifer (Klingler et al., 2020; Martin et al., 2020). The sediment, a poorly consolidated tufa, is a mixture of biogenous carbonate precipitates (~85%)

and organic matter, with an average total organic carbon (TOC) content of 5.7% for the homogenized sediment. Groundwater from the anoxic region of the Ammer aquifer was directly pumped into air-tight bags (Tedlar®, Sigma Aldrich) and used as the inflowing solution, thereby mimicking natural conditions. For further details on the packing procedure and a photograph of the columns see the section Text S1 and Figure S1a in Supporting Information S1.

The experiment was conducted in a temperature-controlled chamber at 12°C, the mean groundwater temperature of the Tufa aquifer. Initially, the columns were allowed to equilibrate with the groundwater for 7 days via a continuous injection at a flow rate of 2 mL hr⁻¹. During the last 100 hr of the equilibration phase, SIP measurements were performed (Figure S2 in Supporting Information S1). Following the equilibration phase, a 10.2 mM NaBr tracer solution was injected over 48 hr at a pumping rate of 2.00 ± 0.16 mL hr⁻¹ (flow velocity, v : 5 cm d⁻¹), to capture the conservative transport of Br⁻ and thereby estimate physical transport parameters. Concentration samples were periodically collected at the outflow (Na⁺, Br⁻ and major ions) of Col-1, in addition to concurrent SIP measurements at all three columns, over 192 hr (8 days).

The tracer injection was followed by a preliminary biostimulation phase in which NaNO₃ (0.5 mmol L⁻¹) and NaLac (0.5 mmol L⁻¹) were injected continuously at varying flow rates. During biostimulation, two columns (Col-1 and Col-2) received the biostimulating solutions whereas the third column served as a control and received unaltered groundwater stock plus ultra-pure water (MilliQ®, Millipore, USA) from the syringe pump. Lactate was added as a primer to enhance and accelerate denitrification and shorten potential lag times of microbial activity (Blagodatskaya & Kuzyakov, 2008). During the preliminary biostimulation phase, the flow rate and nitrate inflow concentration were adjusted until nitrate was detected in outflow samples. This was followed by the main biostimulation phase (henceforth referred to as the biostimulation phase) with an average flow rate and NO₃⁻-concentration of 7.2 mL hr⁻¹ (v : 0.16 m d⁻¹) and 4.0 mmol L⁻¹ over 162 hr (6.75 days), respectively and a lactate concentration of 0.5 mmol L⁻¹. Pore water and outflow samples were collected daily, and SIP measurements were performed every 4 hr. For each sampling event, initially 0.5 mL of pore water were extracted and discarded (dead volume of the sampler), followed by the extraction of 1 mL of sample. Finally, flow was stopped, and the columns were incubated for 840 hr (35 days) under no-flow conditions, yielding a final static phase. During the static phase, pore water samples were taken at a weekly interval to monitor the extent of nitrate reduction, and SIP measurements continued at a 4–8 hr interval. During pore water sampling, the columns were connected to an air-tight groundwater reservoir bag (Tedlar®, Sigma Aldrich) at the inflow and outflow, enabling inflow of groundwater to replace the sampled volume, thus maintaining constant water saturation during the entire phase.

We decided to forfeit direct cell counting and DNA quantification via sacrificial sampling of the sediment because it would have required a prohibitive number of replicates for adequate monitoring of temporal dynamics. Moreover, while preliminary experiments had shown that microbial cells could be successfully detached from the Tufa sediment, reliable cell counting was impeded by the high background fluorescence of the organic matter present in the sediment (see Text S3 and Figure S4 in Supporting Information S1). Therefore, we relied on a DNA quantification during a preliminary nitrate reduction experiment to confirm the presence of denitrification functional genes and the microbial community's capacity to reduce NO₃⁻ (Text S2 and Figure S3 in Supporting Information S1).

2.2. Geochemical Analysis of Pore Water and Outflow Samples

Geochemical analyses of the pore water were conducted on samples collected at the outflow and at both sampling ports (5.6 and 11.6 cm). Prior to analysis, the samples were filtered (0.45 μm), diluted if necessary and stored at 4°C. Major ions were quantified with an ion chromatograph (Metrohm, Germany). Bicarbonate concentrations were estimated by closing the ion balance of major ions. NO₃⁻, NO₂⁻- and NH₄⁺-concentrations were quantified colorimetrically using a continuous-flow analyzer (Seal Analytical Norderstedt, Germany) and lactate concentrations were quantified via high-performance liquid chromatography (HPLC) (Shimadzu Deutschland GmbH, Germany).

2.3. SIP Measurements

SIP spectra were recorded at regular intervals using a measurement script (Störko, 2019) that enabled automation of time series measurements using the Portable SIP Unit (Ontash and Ermac Inc., U.S.). Phase shift ($-\Phi$) and

impedance magnitude ($|Z|$) were measured over 51 log-frequency intervals between 0.01 and 1,000 Hz with a reference resistor of 1,000 Ω and an amplitude of 5 V. The results were converted to apparent, spatially uniform, frequency-dependent complex conductivities via the geometric factor of the given electrode setup. The geometric factor of the electrode set-up was determined experimentally through measurements of the apparent electrical conductivity of the columns filled with water of known conductivity.

2.4. Reactive Transport Modeling

We simulated reactive transport of the solutes through the column via the one-dimensional (1-D) advection-dispersion-reaction equation, accounting for the mass balance of both aqueous and sorbed concentrations for solutes that undergo cation exchange:

$$\frac{\partial C}{\partial t} + \frac{(1 - n_e)\rho_s}{n_e} \frac{\partial S}{\partial t} + v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = R \quad (1)$$

in which C (mmol L^{-1}) and S (mmol g^{-1}) are the aqueous- and solid-phase concentrations for a sorbing compound, respectively, t and x denote the temporal and spatial coordinates, R ($\text{mmol L}^{-1} \text{h}^{-1}$) is the net reaction rate of all microbial transformations, n_e (–) is the effective porosity of the Tufa pack, ρ_s (g L^{-1}) is the mass density of the solids (approximated herein as that of quartz, 2,650 g L^{-1} , which is in the range of values reported for calcite), v (m s^{-1}) is the effective linear velocity, and D ($\text{m}^2 \text{s}^{-1}$) is the dispersion coefficient, calculated from the pore diffusion coefficient (D_p in $\text{m}^2 \text{s}^{-1}$) of each compound and the Tufa-specific dispersivity (α in m), using the approach of Scheidegger (1961): $D = \alpha v + D_p$. Equation 1 is subject to a known flux-boundary condition at the inlet and a zero-dispersive flux boundary condition at the outlet. For solutes that do not undergo cation exchange (i.e., anions) the second term in Equation 1 drops out. An overview of all model parameters and the system of governing equations is provided in Text S4 and Tables S2 and S3 in Supporting Information S1.

The ion exchange between Na^+ and major cations (Ca^{2+} and Mg^{2+}) was simulated via competitive sorption, where reversible sorption rates, $r_{\text{sorb}}^{\text{Na}}$ and $r_{\text{sorb}}^{\text{Me}}$, in $\text{mmol of charge (mmol)} \text{ g}^{-1} \text{ s}^{-1}$, for Na^+ and Me^{2+} (the sum of Ca^{2+} and Mg^{2+}), respectively, were driven by the difference between equilibrium, $S_{\text{Na/Me}}^{\text{eq}}$, and actual, $S_{\text{Na/Me}}$, concentrations of sorbed cations ($\text{mmol}_c \text{ g}^{-1}$). The equilibrium concentrations were computed by solving for the aqueous and sorbed concentrations for a given total amount of solute via a fixed-point (Picard) iteration assuming the following generalized Langmuir isotherm, shown here for the competitive sorption of Na^+ and the sum of divalent cations (Me^{2+}):

$$S_{\text{Na}}^{\text{eq}} = \frac{s_{\text{max}} \cdot C_{\text{Na}}}{C_{\text{Na}} + K_{\text{ads}}^{\text{Na}} \left(1 + \frac{C_{\text{Me}}}{K_{\text{ads}}^{\text{Me}}} \right)} \quad (2)$$

$$r_{\text{sorb}}^{\text{Na}} = \lambda (S_{\text{Na}}^{\text{eq}} - S_{\text{Na}}) \quad (3)$$

$$r_{\text{sorb}}^{\text{Me}} = \lambda (S_{\text{Me}}^{\text{eq}} - S_{\text{Me}}) \quad (4)$$

in which, C_{Na} and C_{Me} ($\text{mmol}_c \text{ L}^{-1}$) are the aqueous phase concentrations of Na^+ and Me^{2+} , respectively, s_{max} ($\text{mmol}_c \text{ g}^{-1}$) is the maximum sorption capacity of the Tufa sediment, and $K_{\text{ads}}^{\text{Na}}$ and $K_{\text{ads}}^{\text{Me}}$ ($\text{mmol}_c \text{ L}^{-1}$) are the binding constants of Na^+ and Me^{2+} , respectively, and λ (s^{-1}) is the kinetic mass-transfer rate constant. An identical formulation for $S_{\text{Me}}^{\text{eq}}$ can be obtained by replacing “Na” terms by “Me” terms and using $r_{\text{sorb}}^{\text{Me}} = -r_{\text{sorb}}^{\text{Na}}$.

Denitrification coupled to the oxidation of both lactate and organic carbon derived from the solid matrix was simulated using Monod kinetics and explicitly considering the biomass of the denitrifying microbial community as an immobile species. We considered a constant cell density and accounted for microbial activation and deactivation in the presence or absence of NO_3^- , via the switch-function approach of Stolpovsky et al. (2011) and Mellage et al. (2015). In natural sediments cell densities are relatively stable, but facets of the microbial community are known to become active in response to the presence or absence of substrates (Lennon & Jones, 2011). Thus, by simulating activation and deactivation our model formulation enables the prediction of active biomass. Denitrification was simulated as a two-step reaction where each electron donor was coupled to the reduction of

nitrate to nitrite and nitrite to N_2 . The rates of denitrification $r_{lac}^{DNO_x}$ ($mmol\ L^{-1}\ s^{-1}$) for the two successive steps are:

$$r_{lac}^{DNO_x} = \frac{\mu_{max}^{NO_x}}{Y_{lac}} \left(\frac{C_{Lac}}{C_{Lac} + K_{Lac}} \right) \left(\frac{C_{NO_x}}{C_{NO_x} + K_{NO_x}} \right) \frac{(1 - n_e)\rho_s}{n_e} BIO_{act} \quad (5)$$

in which $\mu_{max}^{NO_x}$ (s^{-1}) is the maximum specific growth rate constant, Y_{lac} (cells $mmol\text{-}Lac^{-1}$) is the microbial yield coefficient, C_{Lac} ($mmol\ L^{-1}$) the concentration of lactate, K_{Lac} ($mmol\ L^{-1}$) is the lactate half-saturation constant, C_{NO_x} ($mmol\ L^{-1}$) and K_{NO_x} ($mmol\ L^{-1}$) are the concentration and half-saturation constant of NO_3^- ($x = 3$) or NO_2^- ($x = 2$) and BIO_{act} (cells g^{-1}) is cell density of active biomass. To describe the system's response to priming with lactate, we included a release of readily bioavailable dissolved organic carbon (DOC) from the matrix, directly dependent on the concentration of lactate and a first-order hydrolysis rate coefficient, k_{hyd} (s^{-1}):

$$r_{hyd} = k_{hyd}C_{Lac} \quad (6)$$

Here, we assumed that the priming led to an overall increase in microbial activity, thus increasing the hydrolysis of solid organic carbon (SOC) to readily biodegradable DOC that was also available as an electron donor for denitrification. Assuming that the hydrolysis yields a labile DOC that is very bioavailable, the sequential rates of denitrification coupled to DOC oxidation share the same rate coefficients as the lactate-dependent rates:

$$r_{DOC}^{DNO_x} = \frac{\mu_{max}^{NO_x}}{Y_{lac}} \left(\frac{C_{DOC}}{C_{DOC} + K_{Lac}} \right) \left(\frac{C_{NO_x}}{C_{NO_x} + K_{NO_x}} \right) \frac{(1 - n_e)\rho_s}{n_e} BIO_{act} \quad (7)$$

Finally, a lactate-independent denitrification reaction coupled to the oxidation of SOC was implemented. It was formulated as a single Monod rate law due to the high amount of organic carbon in the sediment that was assumed to be non-limiting:

$$r_{SOC}^{DNO_x} = \frac{s\mu_{max}^{NO_x}}{Y_{SOC}} \left(\frac{C_{NO_x}}{C_{NO_x} + sK_{NO_x}} \right) \frac{(1 - n_e)\rho_s}{n_e} BIO_{act} \quad (8)$$

in which $s\mu_{max}^{NO_x}$ (s^{-1}) is the maximum specific growth rate constant for denitrification coupled to SOC, sK_{NO_x} ($mmol\ L^{-1}$) are the half-saturation constant of NO_3^- ($x = 3$) or NO_2^- ($x = 2$) and Y_{SOC} (cells $mmol\text{-}SOC^{-1}$) is the corresponding microbial yield coefficient.

The activation and deactivation rates of the microbial consortium, r_{act} and r_{deact} (cells $g^{-1}\ s^{-1}$), respectively, were modeled using first-order kinetics and scaled via a switch-function, θ (–), that determines the favorability of activation, that is, whether or not electron acceptor (i.e., nitrate) is present:

$$r_{act} = \theta k_{act} BIO_{ina} \quad (9)$$

$$r_{deac} = (1 - \theta) k_{act} BIO_{act} \quad (10)$$

$$\theta = \frac{1}{\exp\left(\frac{C_{NO_3}^{thresh} - C_{NO_3}}{st \cdot C_{NO_3}}\right) + 1} \quad (11)$$

where k_{act} (s^{-1}) is the first-order activation and deactivation rate coefficient and BIO_{ina} (cells g^{-1}) is the cell density of inactive biomass. The switch-function in Equation 11 can take on values between 0, maximally unfavorable conditions, and 1 during optimal conditions. The magnitude of θ depends on the difference between C_{NO_3} and a pre-defined activation threshold nitrate concentration, $C_{NO_3}^{thresh}$. The non-dimensional coefficient st determines the steepness of the transition between the limits of the switch-function (Stolpovsky et al., 2011).

The model was discretized in space by the finite volume method, converting the reactive transport equations to a nonlinear system of ordinary differential equations which was solved in MATLAB using the ordinary-differential-equation solver, ode15s (Shampine & Reichelt, 1997).

2.5. Cole-Cole Model

The Cole-Cole relaxation model (Pelton et al., 1978) is a phenomenological model that parameterizes the frequency-dependent complex resistivity of SIP measurements exhibiting a single spectral peak:

$$\rho^* = \rho_0 \cdot \left(1 - m \cdot \left(1 - \frac{1}{1 + (i \cdot \omega \cdot \tau)^c} \right) \right) \quad (12)$$

where ρ^* (Ω m) is the modeled complex resistivity (i.e., the inverse conductivity), ρ_0 (Ω m) is the DC resistivity, ω (rad) is the angular frequency, m (–) is the chargeability, τ (s) is a time constant related to the peak frequency, and c (–) is the Cole-Cole exponent that describes the broadness of the polarization peak (Pelton et al., 1978).

We extended the Cole-Cole model to account for two parallel charge-storage contributions stemming either from the sediment matrix or from the active microbial community:

$$\rho^* = \rho_0 \cdot \left(1 - \left(m_{\text{mat}} \cdot \left(1 - \frac{1}{1 + (i \cdot \omega \cdot \tau_{\text{mat}})^{c_{\text{mat}}}} \right) + m_{\text{bac}} \cdot \left(1 - \frac{1}{1 + (i \cdot \omega \cdot \tau_{\text{bac}})^{c_{\text{bac}}}} \right) \right) \right) \quad (13)$$

in which all terms have the same meaning as in the single Cole-Cole model but the subscripts “mat” and “bac” refer to the matrix- and bacterial-specific coefficients. In the following we refer to the matrix-related contribution to polarization as $\text{CC}_{\text{matrix}}$ (CC = Cole-Cole) and to the polarization induced by the microbial community as $\text{CC}_{\text{bacteria}}$. The log-transformed parameter values were fitted to the measured spectral responses using the trust-region-reflective algorithm (Coleman & Li, 1996) via the function `lsqnonlin` in Matlab. We constrained the parameter ranges based on the following reasoning. First, we assumed that the parameters defining the spectral shape of the matrix-polarization contribution, τ_{mat} and c_{mat} , should not deviate more than 5% from the mean parameters $\bar{\tau}_0$ and $\bar{c}_0$ of single Cole-Cole fits to the first five spectra measured after the start of the experiment before the NaBr injection. Second, we assumed that the characteristic peak frequency associated with the polarization of bacteria should resemble that of previously reported spectra for bacteria, with a distinct peak around 2–30 Hz (Mellage, Holmes, et al., 2018; Mellage et al., 2019; Rosier et al., 2019; Zhang et al., 2014). Hence, a Cole-Cole exponent c_{bac} greater than 0.5, limiting the broadness of the peak, and a time constant τ_{bac} between 1.13×10^{-2} and 1 s were chosen as constraints for the bacterial term. As an initial guess for all matrix parameters, we used the mean parameters $\bar{\rho}_0$, $\bar{m}_0$, $\bar{\tau}_0$ and $\bar{c}_0$ of a single Cole-Cole fit to the first five spectra after the start of the experiment and before the NaBr injection.

3. Results and Discussion

In the following, we present and discuss the results of both the tracer (NaBr) injection and the biostimulation experiment. For conciseness, we focus our discussion of the biostimulation phase (NO_3^- -injection) on the data collected in Col-1. Wherever possible, without limiting the readability of the figures, the results of the replicate (Col-2) and control column are shown as well. Otherwise, those data are presented in the Supporting Information S1.

3.1. Conservative Tracer Injection

3.1.1. Solute Concentrations

Figure 2 compares breakthrough curves of Br^- and major cations (Na^+ , Ca^{2+} , and Mg^{2+}) at the column outlet (17.3 cm) and time series of the change of the maximum σ' and σ'' , relative to pre-injection values during the NaBr-injection phase, to the results of the reactive transport model. The measured outlet concentrations of Br^- (maximum of 9.6 mmol L^{-1}) agree well with the expected behavior of a conservative compound undergoing advective-dispersive transport (Figure 2a). The fit of the model yields an effective porosity (n_e) of 76% and a dispersivity (α) of 0.4 mm for the homogenized Tufa pack. The high porosity reflects the high content of organic matter (peat) in the sediment (Rezanezhad et al., 2017) and agrees with the Tufa's aquatic sediment-like consistency and microporous structure of the Tufa particles (see Figure S1b in Supporting Information S1).

Relative to Br^- , the arrival of its counter ion Na^+ at the outlet was retarded by approximately 10 hr, with a lower peak concentration of 6.2 mmol L^{-1} . The peak arrival of Na^+ occurred 26.5 hr after the arrival of a pulse of Ca^{2+}

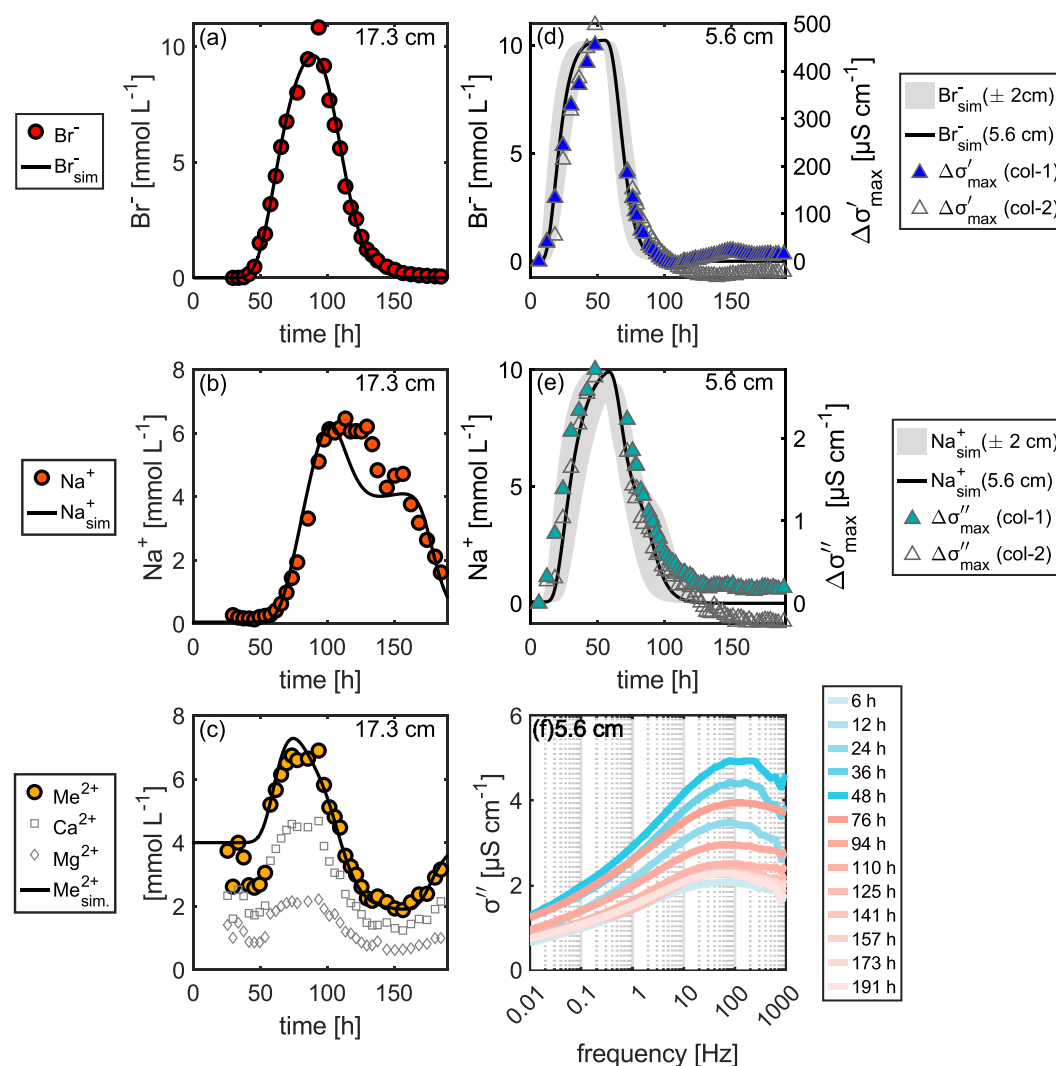


Figure 2. Measured and simulated breakthrough curves at the column outlet, $l = 17.3$ cm, and at the location of the first potential electrode pair ($l = 5.6$ cm); (a, d) Br^- ; (b, e) Na^+ ; (c) Me^{2+} ($\text{Ca}^{2+} + \text{Mg}^{2+}$). The simulated aqueous Br^- and Na^+ concentrations at $l = 5.6$ cm are compared to the measured change (Δ) in σ'_{max} and σ''_{max} in panels (d) and (e). The shaded areas depict the concentration breakthrough at 5.6 ± 2 cm. Time-lapse changes in σ'' spectra at location 5.6 cm in Col-1 are shown in (f).

and Mg^{2+} . Because both Ca^{2+} and Mg^{2+} responded equally to the tracer injection and remained at a relatively constant 2:1 ratio, they are presented and discussed here as their sum, Me^{2+} (Figure 2c). The competitive sorption model was able to accurately capture the timing and extent of Na^+ and Me^{2+} breakthrough. The measured peak Na^+ concentration remained constant for about 30 hr (between 97 and 130 hr) followed by a concentration drop, driven by the shift to NaBr-free solution at the inlet (at 48 hr). The concentration drop exhibited a small shoulder from 137 to 156 hr at 4.7 mmol L^{-1} and a longer tailing than Br^- (Figure 2b). The model predicts a more rapid decrease in concentration after the peak concentration is reached and a more pronounced shoulder from 129 to 161 hr at 4.1 mmol L^{-1} (Figure 2b). We attribute the discrepancy to slight differences in the cation exchange between Ca^{2+} – Na^+ and Mg^{2+} – Na^+ that were neglected in our model formulation.

Concentrations of Ca^{2+} and Mg^{2+} increased due to cation exchange-driven release (Amrhein & Suarez, 1990; Poonia & Talibudeen, 1977; Rahman & Rowell, 1979) in the presence of Na^+ , followed by a concentration drop to about half of the inflow concentration during the reverse reaction as NaBr-free solution was injected. The initial Ca^{2+} and Mg^{2+} concentrations were approached by the end of the tracer injection (Figure 2c) as the remaining Na^+ was released and Ca^{2+} and Mg^{2+} became the dominant species. The ability of the competitive sorption model

to capture the dynamics in cation concentrations confirms that cation exchange, driven by the incoming high Na^+ concentration, caused the replacement of divalent cations by Na^+ in the mineral and organic matter EDLs. The process was reversed once NaBr-free groundwater replaced the tracer solution at the inlet.

3.1.2. SIP Response

The dynamics in the geochemical composition of the pore fluid and surface sites were associated with σ' and σ'' changes. The breakthrough of Br^- caused an increase in the DC electrical conductivity of the pore fluid, and consequently in σ' at the first potential electrode pair ($l = 5.6$ cm), see Figure 2d (for $l = 11.6$ cm, see Figure S5 in Supporting Information S1). The simulated peak concentration of 9.9 mmol L^{-1} at 5.6 cm coincides with an increase in σ' of 455 and $497 \mu\text{S cm}^{-1}$ from a starting value, $\sigma'(t_0)$, of 380 and $440 \mu\text{S cm}^{-1}$ in Col-1 and Col-2, respectively. After 100 hr, the pre-injection level was approached, with σ' stabilizing at $393 \mu\text{S cm}^{-1}$ in Col-1 and $420 \mu\text{S cm}^{-1}$ in Col-2. In general, both columns showed consistent σ' dynamics that agree well with the simulated breakthrough of Br^- -ions, the ion that dominated the changes in pore water conductivity. Potential electrode pairs measure integrated SIP signals over an electrode response volume, determined by the geometry of the setup (Mellage, Holmes, et al., 2018). Thus, while the major contribution is expected to stem from the midpoint of the electrodes, measurements inherently contain contributions from a spatial interval. Hence, we compare SIP measurements to breakthrough concentrations at the midpoint of the electrodes and at the midpoint ± 2 cm. The range is shown as the shaded gray area in Figures 2d and 2e.

We observed an increase in the maximum σ'' of up to $2.8 \mu\text{S cm}^{-1}$ as Na^+ arrived at 5.6 cm (Figure 2e). Similarly, the tailing of σ'' matched the simulated drop in aqueous Na^+ concentration. The temporal changes of simulated aqueous Na^+ concentrations and σ'' coincide and are consistent between Col-1 and Col-2. The increase in σ'' is driven by the higher surface mobility of Na^+ in the EDL relative to Ca^{2+} and Mg^{2+} (Ben Moshe et al., 2021). Analogous to the σ' , σ'' approached pre-injection levels after the NaBr injection, leveling off at 2.27 and $2.67 \mu\text{S cm}^{-1}$ in Col-1 and Col-2, respectively. A carbonate dominated system like the Tufa is susceptible to precipitation-dissolution processes that can be induced by several factors, for example, changing cation or bicarbonate concentrations and subtle pH changes (Morse et al., 2007; Tamir et al., 2012) that can influence the pore-fluid and EDL composition and thus SIP signals. The experimental setup herein was designed to minimize these secondary contributions (e.g., by using groundwater from the same site as the sediment and storing the collected groundwater in gas-tight bags to maintain the CO_2 partial pressure) and it is thus beyond the scope of this work to quantify them. The excellent agreement of the competitive sorption model with the cation breakthrough suggests that carbonate dissolution played only a minor role. However, it may explain the small differences in the SIP signals before and after tracer injection.

Despite the considerable changes in σ'' , the cation exchange process did not exhibit a strong influence on the spectral shape of σ'' . In Figure 2f, σ'' spectra are shown for different time-points during the tracer injection in Col-1 at 5.6 cm from the inlet (spectra of the other columns and at 11.6 cm are shown in Figures S7b, S7c, S8b, and S8c in Supporting Information S1). The sediment has a background polarization between 0.7 and $2 \mu\text{S cm}^{-1}$. It increases steadily toward higher frequencies, reaching a broad peak at around 50–400 Hz, and decreases toward 1,000 Hz. During the NaBr injection, variations in σ'' exhibited the same general trend at all frequencies. There was no development of a clear peak nor a shift in peak frequency. At the end of the NaBr-injection, σ'' spectra approached the pre-injection magnitude, highlighting the reversibility of the cation-exchange process. The phase shift of the Tufa ranged between 1.7, at low frequencies, and 6.2 mrad at peak frequencies and reached up to 8.7 mrad during the NaBr injection (Figures S9, and S10a–S10c in Supporting Information S1).

In silica- and mineral dominated-porous media, that is, devoid of organic matter, Vaudelet et al. (2011), Hao et al. (2015) and Mellage et al. (2022) showed that changes in surface-associated ion concentrations are proportional to σ'' -changes. In contrast, the σ'' -dynamics, herein, did not entirely reflect changes in sorbed Na^+ concentrations (Figure S6b in Supporting Information S1), but rather more closely traced the presence of Na^+ in the aqueous phase (Figure 2e). In organic-matter-containing soils, as is the case for the Tufa sediment, Mellage et al. (2022) showed that while σ'' does change in response to sorption, changes are not proportional to sorbed concentrations (therein, of a divalent organic cation). We speculate, that in a more complex organic-matter-containing matrix, like the Tufa, poorly-understood polarization mechanisms in the organic matter (Katona et al., 2021; Mellage et al., 2022), drive the observed discrepancy. Thus, suggesting that the relationship between σ'' and counter ions in the EDL, under temporally variant geochemical conditions, may in fact be more complex than previously thought, especially in natural sediments with different types of sorption sites/polarizable media. Nevertheless, our

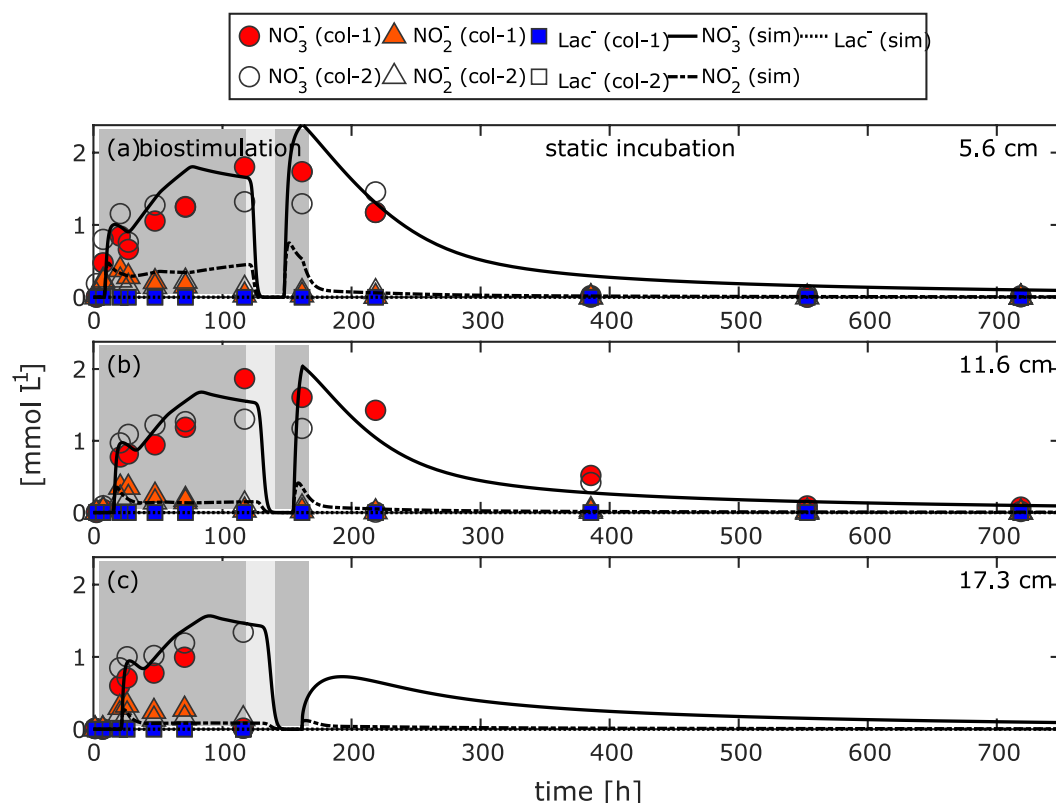


Figure 3. Concentration time series of NO_3^- , NO_2^- and lactate (Lac^-) during the biostimulation phase (gray background) and the static phase (white background) alongside the simulated concentrations at 5.6 cm (a), 11.6 cm (b) and at the outlet (c), $l = 17.3$ cm from the inlet. The light gray area separating the biostimulation phase denotes the 22 hr interruption in NO_3^- and lactate injection.

competitive sorption model sheds light on the geochemical variations that drive the SIP response in Tufa sediment during ion-exchange brought on by the injection of higher concentrations of monovalent ions and provides the basis for modeling bio-reactive transport during the biostimulation phase.

3.2. NO_3^- -Biostimulation

In the following, we present the results of the biostimulation and the static incubation phases. During the preliminary biostimulation phases, neither NO_3^- , NO_2^- nor lactate was detected at any measurement location, indicating that denitrification took place in the first few cm at the column inlet. The corresponding concentration time series and SIP spectra of the preliminary flow phases are presented in Figures S11, S7e, S7f, S8, and S8f in Supporting Information S1. Geochemical data (i.e., major ions, pH and electrical conductivity) of the preliminary biostimulation phase and the main biostimulation phase are summarized in Figure S12 in Supporting Information S1.

3.2.1. Solute Concentrations

The biostimulation phase was initiated by an increase of the flowrate to 8.0 mL hr^{-1} ($v: 0.18 \text{ m d}^{-1}$) and of the NO_3^- -concentration to 2 mmol L^{-1} . It lasted for 162 hr and was followed by 840 hr of static incubation. Figure 3 presents measured and simulated breakthrough curves of NO_3^- , NO_2^- , and lactate at 5.6, 11.6 cm, and the outflow during both phases. NO_3^- -breakthrough at 5.6 cm from the inlet was observed within 20 hr at around 50% of the inflow concentration, that is, 0.9 and 1.2 mmol L^{-1} in Col-1 and Col-2, respectively (Figure 3a). Concentrations of NO_3^- then increased up to 1.8 and 1.3 mmol L^{-1} at 117 hr NO_2^- accumulated up to 0.39 mmol L^{-1} 21 hr after the beginning of the biostimulation, followed by a decrease to less than 0.03 mmol L^{-1} .

During the biostimulation phase, aging of the tubing altered the ratio between the inflowing groundwater pumped via the peristaltic pump and the reactant-containing solution injected via the syringe pump. This resulted in a

constantly decreasing flow rate and a consequent increase in the injection concentrations of NO_3^- and lactate to 5 and 1.6 mmol L^{-1} , respectively. We accounted for this in our reactive transport model by implementing changing boundary conditions at the inflow (see Figure S13 in Supporting Information S1). The reactive transport model was fitted to the average concentrations of both columns. It captures the concentration breakthrough during denitrification quite well. After lactate was consumed within the uppermost centimeters close to the inlet, denitrification had to be coupled to the oxidation of organic material released from the sediment matrix. We found that an additional source of readily bioavailable organic carbon, yielding high denitrification rates only in the first centimeters, was required to predict the N-concentrations. Therefore, we implemented a lactate-dependent release of DOC as a result of enhanced hydrolysis of organic matter due to the priming with lactate (Blagodatskaya & Kuzyakov, 2008). From 119 to 142 hr (shown as a light gray background in Figure 3), the injection of NO_3^- and lactate stopped due to a technical problem. After this interruption, the biostimulation was resumed for another 20 hr until the pore water contained NO_3^- again.

The rise in NO_3^- upon re-injection was captured by the model at 11.6 cm, but slightly over-predicted at 5.6 cm. Similarly, during the static incubation (from 162 hr onwards in Figure 3), NO_3^- was consumed in less than 223 and 393 hr at 5.6 and 11.6 cm from the inlet, respectively, whereas the model predicts a more gradual decline, in particular, at 5.6 cm. The measured and modeled discrepancies suggest a more pronounced depth-distribution of denitrification activity in the columns than accounted for in our model. We attribute this to the additional influence of the continued priming effect of lactate at the inlet. Nevertheless, our model is able to predict differences in denitrification rates with depth and overall, captures the temporal dynamics of both columns throughout both incubation phases accurately. The mean model computed denitrification rates were 285 versus 200 $\mu\text{mol L}^{-1} \text{d}^{-1}$ at 5.6 and 11.6 cm, respectively. The rates are 2–20 times higher than zeroth-order denitrification rates determined at different field sites without the presence of highly concentrated electron donors (Green et al., 2008; Tesoriero & Puckett, 2011) and on the order of field-derived denitrification rates in a riparian zone (Tesoriero & Puckett, 2011). Given the high content of organic carbon of 5.7% in this sediment, the resulting denitrification rates are reasonable and demonstrate that experimental conditions were close to natural field conditions.

3.2.2. SIP Response

Figure 4 presents a subset of the spectral signal changes in σ'' , recorded during the biostimulation and static incubation phases in Col-1 at the 5.6 cm electrode pair, along with the temporal variations in the maximum σ'' (σ''_{max}) in Col-1 and Col-2 compared to the simulated fraction of active biomass. A more detailed summary of σ'' -spectra measured in all columns is presented in Figures S7 and S8g–S8l in the Supporting Information S1.

The σ'' -spectra in Figures 4a and 4b show that the charge storage in the Tufa pack increased during the biostimulation phase. These variations were most evident in the frequency range of 1–100 Hz. Compared to the spectra during the conservative-tracer injection (Figure 2f), the spectrum directly before the start of the (main) biostimulation phase (labeled $t = -1$ hr in Figure 4a) exhibited a different shape. The measured response developed a clear peak, with a maximum of 3.3 $\mu\text{S cm}^{-1}$ at 3 Hz. In Col-1, the peak developed during the preliminary biostimulation phase (Figure S7d in Supporting Information S1), which already saw NO_3^- being injected, whereas in Col-2 the peak was absent in the preliminary phase (Figure S7e in Supporting Information S1) but appeared after ~ 30 hr during the main biostimulation phase (Figure S7h in Supporting Information S1). Despite these subtle differences, the two replicates exhibited similar overall trends and polarization magnitudes.

The control column showed a minor increase in σ'' during the preliminary biostimulation phase of 0.9 $\mu\text{S cm}^{-1}$ and then of 0.5 $\mu\text{S cm}^{-1}$ during the main biostimulation phase reaching a peak value of 3.6 $\mu\text{S cm}^{-1}$ at 100 hr (Figures S7f and S7i in Supporting Information S1). This increase was only observed at 5.6 cm, at 11.6 cm σ'' remained constant (Figures S8f and S8i in Supporting Information S1). Sulfate, present in the groundwater stock, was continuously injected into the columns at a concentration of $\sim 0.18 \text{ mmol L}^{-1}$. The increase of σ'' in the control coincided with a drop in sulfate concentrations (Figure S14 in Supporting Information S1). We speculate that it was used as an electron acceptor in the absence of nitrate (Miao et al., 2012), yielding the measured increase in SIP signals at 5.6 cm in the control column. This is also justified by the much less pronounced SIP-signals relative to the treated columns, in line with sulfate being a much lower energy-yielding electron acceptor.

The observed trends in the spectral responses translated to an increased σ''_{max} in both replicate columns (Figure 4c) of up to 2.4 $\mu\text{S cm}^{-1}$ at 108 hr, reaching magnitudes of 5.4 and 5.9 $\mu\text{S cm}^{-1}$ in Col-1 and Col-2, respectively (the corresponding phase shifts were 13.0 mrad in Col-1 and 12.3 mrad in Col-2, see Figure S9g and S9h in Supporting

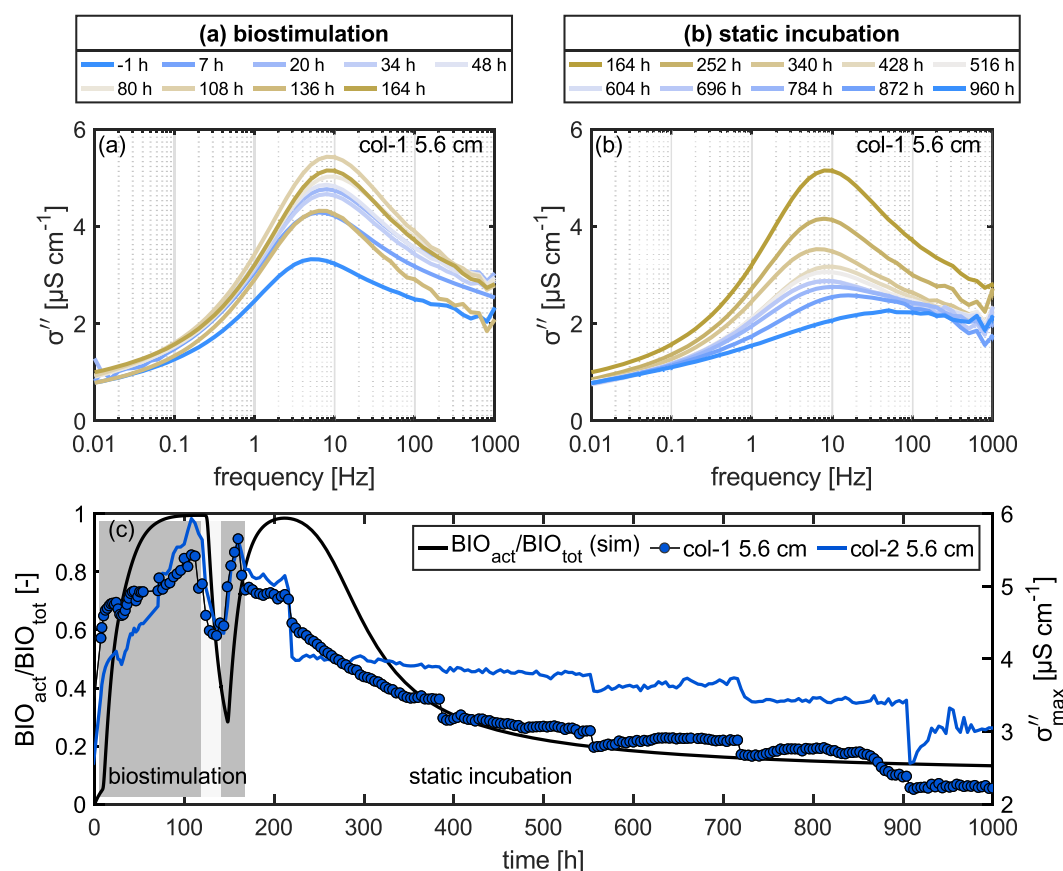


Figure 4. Selected spectra at 5.6 cm in Col-1 during (a) the biostimulation phase and (b) the static incubation phase. The fraction of simulated active biomass is compared to the maximum imaginary conductivity, σ''_{max} , at 5.6 cm in Col-1 and Col-2 in panel (c).

Information S1). Conversely, the real component of the complex conductivity, σ'_{max} , was approximately constant after the first 10 hr (e.g., $414.1 \pm 24.2 \mu\text{S cm}^{-1}$ in Col-1) of the biostimulation phase (see Figure S15c in Supporting Information S1). The 22 hr period in which no NO_3^- was injected yielded a clearly visible drop in σ''_{max} of $1\text{--}1.6 \mu\text{S cm}^{-1}$, followed by a recovery in the last 20 hr of the biostimulation phase. After stopping flow, which led to the gradual consumption of NO_3^- (Figure 3), σ'' decreased approximately exponentially by $1.9\text{--}2.9 \mu\text{S cm}^{-1}$ at all measurement locations until stabilizing after 500 hr. Once all NO_3^- was consumed the shape of the σ'' spectra shifted back to that measured during the abiotic tracer injection, that is, prior to biostimulation (Figure 4b). Thus, highlighting the full reversibility of the additional polarization contribution during microbial activity. Pore-water sampling caused drops in σ'' that were less evident during the biostimulation flow phase but resulted in irreversible stepwise changes during the static incubation. We speculate that these alterations were brought on by abrupt variations of the pore-water chemistry which were “washed out” in the presence of flow. During the static incubation phase σ' (see Figure S15d in Supporting Information S1), followed the trend of σ'' . However, the relative decrease in σ' was less pronounced (-23% to -33%) than that of σ'' (-35% to -52%).

The frequency range of the peak σ'' during biostimulation observed herein agrees well with the frequency range reported for bacteria (Mellage, Holmes, et al., 2018; Mellage et al., 2019; Rosier et al., 2019; Zhang et al., 2014). Moreover, the reversibility of the distinct spectral characteristics after the bio-reactive phase point to a secondary, microbial contribution to our measured polarization responses. The agreement between the temporal trends in σ''_{max} and the simulated fraction of active biomass (Figure 4c), computed based on the fit of the reactive transport model to the geochemical breakthrough curves, provides further evidence to suggest that the unique spectral characteristics and changes in σ'' during biostimulation were brought on by the actively denitrifying microbial community in the Tufa sediment. However, the NaBr-injection showed that changes in pore-fluid conductivity and geochemical composition alter the Tufa's σ'' . Therefore, to uniquely attribute changes in the magnitude of

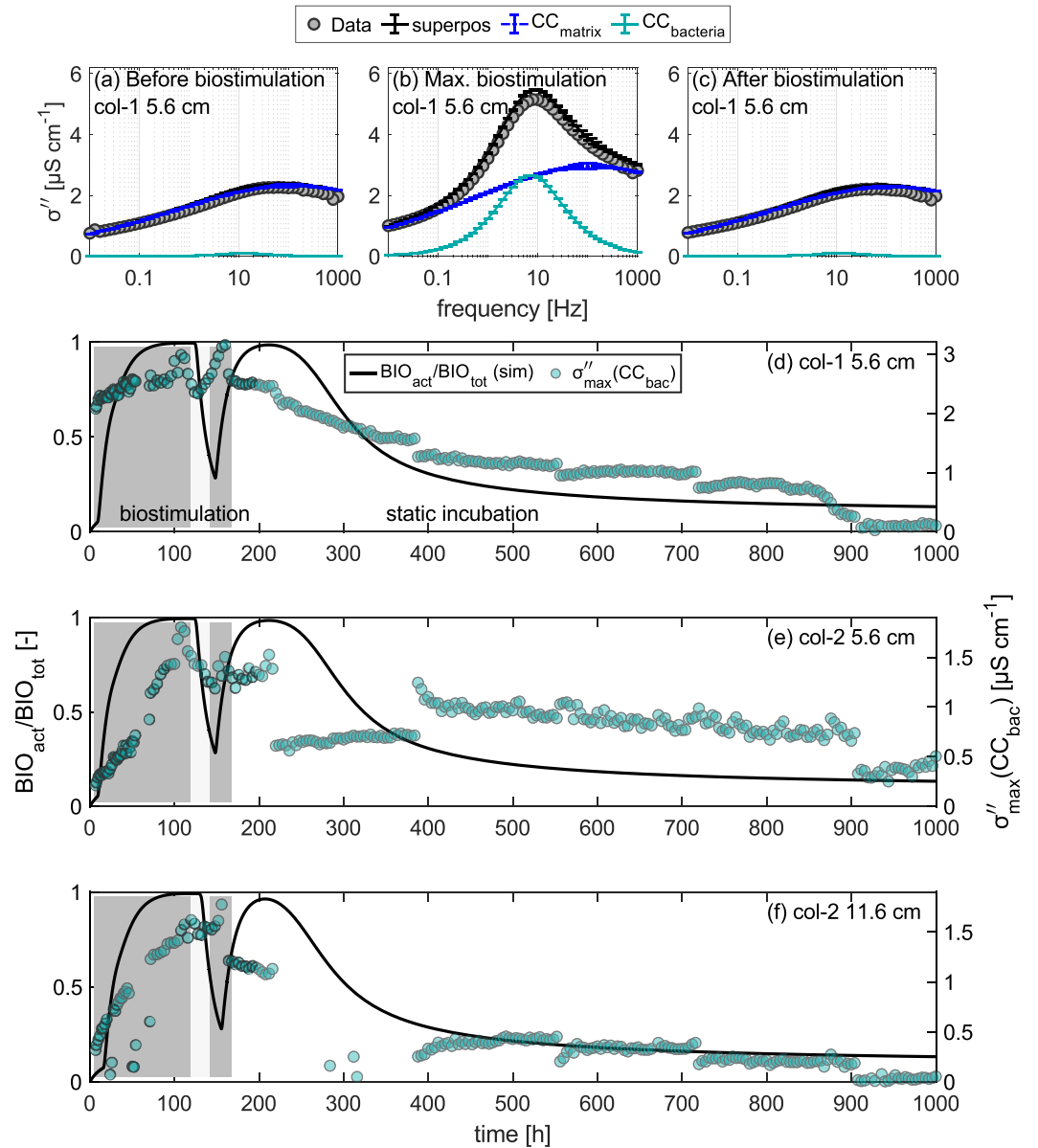


Figure 5. Cole-Cole decomposition of three example spectra recorded in Col-1 at 5.6 cm, before (a), at the peak of biostimulation (b) and after biostimulation (c), where $\text{CC}_{\text{matrix}}$ and $\text{CC}_{\text{bacteria}}$ are the separate sediment and microbial contributions to the polarization signal. The simulated fraction of active biomass $\text{BIO}_{\text{act}}/\text{BIO}_{\text{tot}}$ is compared to the σ''_{max} of the microbial Cole-Cole term during the biostimulation and the static incubation at 5.6 cm in Col-1 (d) and Col-2 (e) as well as at 11.6 cm in Col-2 (f).

σ'' -maxima to microbial activity (Na^+ was injected as a counter ion during biostimulation), in the following, we separate parallel polarization contributions stemming from the EDL of the matrix and that of the microbes via a Cole-Cole decomposition.

3.2.3. Superimposed Polarization Mechanisms

In the following, we make use of the full spectral information to facilitate the direct interpretation of microbially-driven SIP responses. To this end, we apply a Cole-Cole decomposition approach to quantify the contribution of parallel polarization mechanisms to the overall SIP response.

Figure 5 shows the two-term Cole-Cole fit for three spectra, recorded before the first NO_3^- -injection (Figure 5a), at the peak of biostimulation (Figure 5b) and at the end of the static incubation phase (Figure 5c). In all three

cases the superposition of matrix (Tufa sediment) and bacterial contributions adequately fit the behavior of the SIP data, with a slight overestimation during the phase of maximum denitrifying activity.

Before and after the biostimulation, the Cole-Cole decomposition attributed the polarization to the matrix component, CC_{matrix} only. As expected, charge storage during the NaBr-injection was solely attributed to CC_{matrix} , that is, no microbially-driven SIP signature was observed prior to biostimulation (Figures S16 and S18a–S18c in Supporting Information S1). During biostimulation, CC_{matrix} increased by approximately $0.5 \mu\text{S cm}^{-1}$, which was expected due to the co-injection of Na^+ as the counter ion of NO_3^- , but a major part of the change compared to the pre-biostimulation spectra was attributed to CC_{bacteria} . At the peak frequency of the bacterial polarization, 6 Hz, the Cole-Cole decomposition predicted that matrix and bacteria contribute to a similar extent to the overall magnitude of charge storage. The latter highlights that the polarization of cell surfaces can play a significant role in natural sediments despite their small volume fraction.

After separating the bacterial polarization from the matrix polarization, we compare simulated microbial dynamics with the $\sigma''_{\text{max}}(CC_{\text{bacteria}})$ time series in Figures 5d–5f at 5.6 cm in Col-1 (d) and Col-2 (e) as well as at 11.6 cm in Col-2 (f). Indeed, there is a good match between $\sigma''_{\text{max}}(CC_{\text{bacteria}})$ and the model-predicted evolution of active biomass at the different SIP measurement locations during the biostimulation and, to lesser extent, in the static phase. The reactive transport model was fitted to the measured solute concentrations only, thus the good agreement in the trends between active biomass and $\sigma''_{\text{max}}(CC_{\text{bacteria}})$ provides a validation of our conceptual assumption that the polarization peak that we observed during the biostimulation was caused by microbial activity. While microbiological data, such as the quantification of functional genes and transcripts, could have further supported the relationship between σ'' and microbial activity, we chose to rely on concentration time series of duplicate columns rather than on an experimental setup that would allow sacrificial sampling for molecular-biological analyses. The unknown kinetics and long experimental run time would have required a series of ca. 10 columns per replicate (30 in total), making such an experiment unfeasible. Monod-type models based on concentration measurements have been shown to be equally good at predicting denitrification rates as gene-explicit models that incorporate molecular biological data (Störiko et al., 2021). We are, therefore, confident that our model yields an adequate representation the relative changes in microbial activity during our experiment.

Col-1 and Col-2 showed consistent temporal σ'' dynamics, but we also observed features that are not represented by the active biomass predicted by our reactive transport model. We attribute this to two main factors. First, the model does not account for the preliminary biostimulation phase and its effect on the level of microbial activity. The influence of antecedent biostimulation effects was particularly apparent in Col-1. Second, the pore water sampling exerted a strong effect on σ'' that caused marked offsets, especially at the beginning of the static incubation phase, particularly in Col-2.

Overall, the relative temporal dynamics of $\sigma''_{\text{max}}(CC_{\text{bacteria}})$ are similar to the measured σ''_{max} (Figure 4c) confirming that σ'' changes were dominated by microbial activity during denitrification. The most apparent difference between σ''_{max} and $\sigma''_{\text{max}}(CC_{\text{bacteria}})$ is the response to the 20 hr without the injection of NO_3^- . The decrease in CC_{bacteria} by up to $0.6 \mu\text{S cm}^{-1}$ corresponds only to 26%–48% of the change in σ''_{max} . Thus, the Cole-Cole decomposition attributes a major part of the total decrease in σ''_{max} to the cation exchange on the matrix given that also Na^+ was not injected over the 20 hr period (Figure S20 in Supporting Information S1). This suggests that the effect on the activity of the microbial community is less strong, though still significant, than predicted by the reactive transport model or from interpreting the σ''_{max} data only. The removal of the simultaneously changing matrix polarization enables us to access the actual microbial polarization magnitudes, the relevant quantity for a future establishment of quantitative petrophysical relationships between σ'' and microbial abundance and activity in different sediments or for different reactions.

The response of CC_{bacteria} to the absence of substrate is immediate, compared to the simulated active biomass. We speculate that the delayed response of the biomass activation is rather an artifact of the model and that the microbial response to NO_3^- -concentration changes might be much faster. As already pointed out during the discussion of the model fit to the concentration measurements, the model underpredicts denitrification in the last 20 hr of biostimulation, suggesting that the time lag for responses of bacteria to changes in the nutrient supply may be significantly faster, such as the change in $\sigma''(CC_{\text{bacteria}})$, than currently predicted by the model.

The sensitivity of SIP to the activation of microbes may be explained by the microbes' ability to actively alter the structure of their cell wall and surrounding medium. During the energy metabolism of cells, an electrical potential between the extracellular matrix and the cytoplasm is formed by gradients of H^+ or Na^+ ions across the

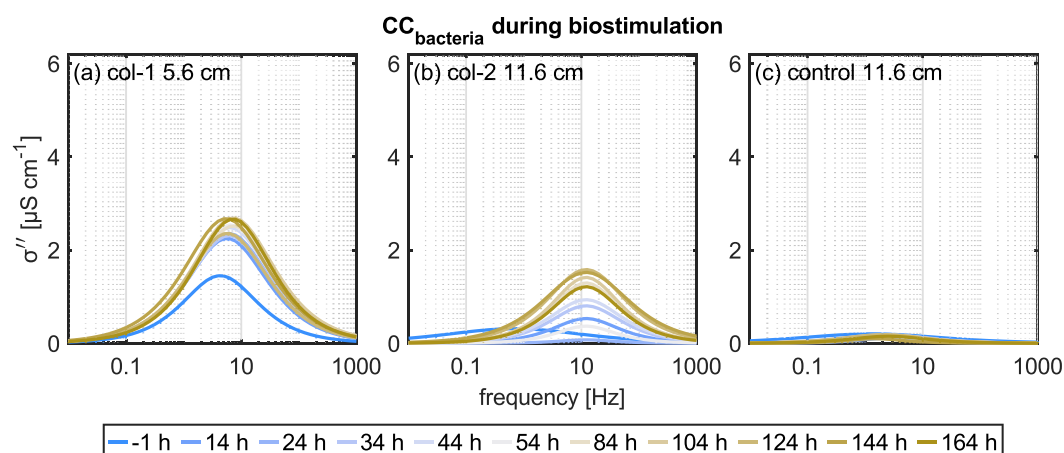


Figure 6. The Cole-Cole term that is associated with bacterial activity, $CC_{bacteria}$, is shown for specific timepoints during the main biostimulation phase in Col-1 at 5.6 cm (a), Col-2 at 11.6 cm (b) and in the control column at 11.6 cm (c).

cell membrane (Maloney et al., 1974). Bacteria can actively influence this gradient through their cell proteins (Konings et al., 2002) and are therefore also actively influencing the composition of the surrounding fluid. In addition, a large fraction of the cell membrane proteins, that can form up to 60% (w/w) of the cell membrane, are involved in solute transport processes, for example, using the H^+ or Na^+ gradients or ATP to actively transport substrates into or out of the cell (Konings et al., 2002). Since these active transport processes require energy, they depend on the activity of the microbes. The macroscopically observable polarization may thus not only be a function of the microbial abundance, but also the metabolic activity. Within the duration of our experiment, we did not expect significant changes in microbial abundance but definitely in their activity, as implemented in the reactive transport formulation. Consequently, we attribute the σ'' -signal to changes in microbial activity. In particular, the immediate response of σ'' to the stop and restart of the NO_3^- -injection points to a fast adaptation of the microbial community to changes in substrate concentrations rather than microbial decay and regrowth as the main influence on polarization. Thus far, this aspect has not been considered in the experimental design and interpretation of microbial SIP studies, but provides an explanation for the difference in polarization magnitude between studies that investigated microbial signals in the absence of reaction (and thus activity) (Abdel Aal et al., 2010; Zhang et al., 2014) to those in the presence of substrates (Joo et al., 2021; Mellage, Holmes, et al., 2018; Mellage et al., 2019; Rosier et al., 2019). In the absence of nutrients, reported σ'' changes are less than $1 \mu S cm^{-1}$, whereas σ'' changes over several $\mu S cm^{-1}$ have been observed in the presence of energy-yielding substrates, analogous to the signals recorded herein. We stress that at this state, the relative contributions of microbial abundance and activity as well as their effects on microbe polarization remain unknown, but that our work points toward a significant influence of metabolic activity on polarization that should be considered in future studies.

Figure 6 compares the $CC_{bacteria}$ spectra during the biostimulation phase between the top half of Col-1 (a), the bottom half of Col-2 (b), and the control column (c). Given that the columns were packed and treated in the same way (with the exception of the control not receiving NO_3^-), the results of the Cole-Cole decomposition should yield consistent results across all columns and the different measurement locations. Indeed, distinct differences, reflecting the intensity of bio-activity, are visible. Thus, the Cole-Cole decomposition of the SIP response may provide a means to quickly identify zones and times of high bio-activity independent of concentration data. The approach also enabled the identification of microbial activity in the upper half of the control column, related to sulfate reduction (Figure S14b in Supporting Information S1).

During the static incubation, the decomposition approach attributed the decrease in polarization to both the matrix (Figure S20 in Supporting Information S1) and the bacteria (Figures 5d–5f). In the static phase in general, the fitting was more challenging as the spectra started to show increasing noise at high frequencies likely due to aging of the electrodes toward the end of the experiment. Additionally, pore-water sampling altered the polarization of the matrix significantly and permanently under no-flow conditions, causing, for example, $CC_{bacteria}$ to be zero in Col-2 at 11.6 cm between two sampling events, at 215 and 384 hr (Figure 5f). Thus, we regard the Cole-Cole decomposition during the static phase to be strongly affected by data quality issues that hindered a robust parameter estimation and hence the interpretation of temporal dynamics is limited.

Cole-Cole model parameters have been shown to be highly correlated making parameter interpretation a challenge (Bérubé et al., 2017; Fiandaca et al., 2018). By reconvertng the parameters into complex conductivity values, ambiguities in parameter estimation can be reduced because a subset of parameters is interpreted jointly. The high correlation between the parameters also causes challenges during parameter estimation. For the two-term Cole-Cole model it was therefore necessary to constrain the single parameters based on prior knowledge as described in Section 2.4. Nonetheless, the root-mean square error (RMSE) increased with an increase of CC_{bacteria} , ranging between 0.1 and 0.35 $\mu\text{S cm}^{-1}$ during the main biostimulation phase (Figure S21a in Supporting Information S1). Model uncertainty estimates based on the covariance matrix of the parameters, derived via linear uncertainty propagation, yielded either unrealistically low (during the biostimulation phase, Figure S21b in Supporting Information S1) or extremely high uncertainties, in particular during the static incubation. For the demonstration of the separation of polarization processes within this work, the applied uncertainty analysis provided sufficient information on the reliability of the Cole-Cole decomposition during the different phases. For a future exploration of quantitative relationships between CC_{bacteria} and microbiological data and models, a more rigorous posterior uncertainty quantification, for example by Markov-Chain Monte-Carlo methods, will be necessary.

4. Summary and Conclusions

This study has shown that SIP is sufficiently sensitive to microbial activity to enable monitoring of bio-reactive processes such as microbial denitrification under conditions that are comparable to those found at natural field sites, in terms of sediment and pore-fluid composition, reaction rates, and temperature. With heterotrophic denitrification, we chose a reactive process that does not involve precipitation or dissolution of polarizing minerals such that changes in charge storage could exclusively be attributed to changes in pore-water chemistry and/or microbial activity. In the biostimulation phase of our denitrification experiments, the observed changes in the SIP signal were dominated by microbial activity within the sediment columns, despite the presence of polarization processes by the background matrix. This conclusion is supported by multiple lines of evidence, namely, (a) a reactive transport model that captures the observed concentration time series and predicts maximum microbial activity at times of maximum increase in the imaginary conductivity magnitude, and (b) a decomposition of the complex-conductivity spectra that largely associates the increase in σ'' during biostimulation to a component that differs in its spectrum from that observed in the NaBr-injection phase, when the entire SIP-response was attributed to the change of pore-water chemistry.

We were successful at isolating the contribution of microbial processes from other parallel processes that might contribute to overall charge storage. The NaBr injection showed that alternative processes, for example, cation exchange can also cause an increase in σ''_{max} that might easily be misinterpreted. We propose an easy-to-implement Cole-Cole decomposition approach that helps to discriminate between parallel polarization contributions. The Cole-Cole decomposition successfully differentiated between microbially active and microbially inactive zones and times throughout our experiment. It allowed us to isolate the spectral contribution of a natural microbial community to σ'' , facilitating the determination of the expected magnitude of microbially-driven polarization under varying conditions. Moreover, it can potentially provide information that is necessary for a quantitative comparison of different bio-reactive studies in natural sediments. We found an excellent agreement between the fraction of active biomass and the σ''_{max} determined by the Cole-Cole decomposition during biostimulation and the spectral responses recorded here agreed with σ'' -spectra of single-strains in non-polarizing media (Mellage, Holmes, et al., 2018; Mellage et al., 2019; Rosier et al., 2019; Zhang et al., 2014). Further experiments that focus on the activation-deactivation pattern of microbes might reveal the potential of incorporating SIP data into reactive transport models for the quantitative estimation of microbial kinetic parameters such as the maximum specific growth rate constants and the activation/deactivation rate laws and coefficients.

Our Cole-Cole decomposition only requires the complex conductivity spectrum of the material prior to biostimulation and microbial conductivity spectra from other studies but no (site-specific) geochemical data are necessary to constrain the parameters. This opens new avenues for the application of SIP as a fast method to monitor a system's reactivity without the need to wait for geomicrobiological analysis. However, a rigorous uncertainty estimation and improved parameter optimization is required for improving the quantitative potential of the approach. In particular, Bayesian methods may be well suited to reliably assess the posterior parameter distribution. Finally, the approach would benefit, in future, from a detailed validation coupled to monitoring of microbiological markers including molecular-biological measurements of microbial activity.

Further development of the Cole-Cole decomposition approach may pave the way for the application of SIP as a real-time monitoring method in biogeochemical laboratory experiments. This is of particular value for reaction monitoring during experiments to inform the timing of geochemical sampling. In biotechnology studies, the potential of SIP as a process monitoring method is gaining increasing interest and has shown to have advantages in terms of transferability between different strains and conditions over traditional methods (Slouka et al., 2016, 2017; Turick et al., 2019).

With a frequency range of around 1–100 Hz, microbial polarization occurs within a range that is less prone to measurement errors of SIP (Dahlin et al., 2002; Pelton et al., 1978; Zimmermann et al., 2008), thus facilitating its potential for monitoring in the field. Enhanced in situ denitrification projects like that of Critchley et al. (2014) could benefit from SIP monitoring, providing information on the duration of the “conditioning” phase by detecting the onset of microbial activity from the SIP response. Multi-electrode SIP measurements and associated inversion may be used to locate microbial stimulation in the subsurface. For a better separation of microbial activity from other processes that influence complex conductivity in the subsurface, measurements over the entire frequency range, a spectral decomposition, a careful consideration of measurement errors, and further technological developments will be necessary.

Data Availability Statement

The SIP data, the geochemical data and the Matlab codes for the reactive transport modeling as well as the Cole-Cole fitting are available at <https://doi.org/10.5281/zenodo.7032328> under the international Creative Commons license CC-BY-NC 4.0 (Strobel et al., 2022).

Acknowledgments

Adrian Mellage would like to acknowledge the financial support of the Baden-Württemberg Stiftung received for this project via the Eliteprogramme for Postdocs as well as the financial support of the Ministry for Science, Research and the Arts of Baden-Württemberg via the Research Seed Capital Program (RiSC). We thank Franziska Schädler, Verena Nickeleit and Monika Hertel (University Tübingen) for their support with chemical analysis, Aleksandra Pienkowska for support with qPCR measurements and Bernice Nisch for support with TOC measurements. The authors gratefully acknowledge the Tübingen Structural Microscopy Core Facility (Funded by the Federal Ministry of Education and Research (BMBF) and the Baden-Württemberg Ministry of Science as part of the Excellence Strategy of the German Federal and State Governments) for their support and assistance in this work, and the German Research Foundation DFG (INST 37/1027-1 FUGG) for financial support provided for the acquisition of the cryogenic focused ion beam scanning electron microscope. We thank Jeremiah Shuster and Stefan Fischer for their help with sample preparation and SEM imaging. Open Access funding enabled and organized by Projekt DEAL.

References

- Abascal, E., Gómez-Coma, L., Ortiz, I., & Ortiz, A. (2022). Global diagnosis of nitrate pollution in groundwater and review of removal technologies. *Science of the Total Environment*, 810, 152233. <https://doi.org/10.1016/j.scitotenv.2021.152233>
- Abdel Aal, G. Z., Atekwana, E. A., Rossbach, S., & Werkema, D. D. (2010). Sensitivity of geoelectrical measurements to the presence of bacteria in porous media. *Journal of Geophysical Research*, 115(G3), G03017. <https://doi.org/10.1029/2009JG001279>
- Abdel Aal, G. Z., Atekwana, E. A., Slater, L. D., & Atekwana, E. A. (2004). Effects of microbial processes on electrolytic and interfacial electrical properties of unconsolidated sediments. *Geophysical Research Letters*, 31(12), L12505. <https://doi.org/10.1029/2004GL020030>
- Abdel Aal, G. Z., Slater, L. D., & Atekwana, E. A. (2006). Induced-polarization measurements on unconsolidated sediments from a site of active hydrocarbon biodegradation. *Geophysics*, 71(2), H13–H24. <https://doi.org/10.1190/1.2187760>
- Amrhein, C., & Suarez, D. L. (1990). Procedure for determining sodium-calcium selectivity in calcareous and gypsiferous soils. *Soil Science Society of America Journal*, 54(4), 999–1007. <https://doi.org/10.2136/sssaj1990.03615995005400040011x>
- Atekwana, E. A., & Slater, L. D. (2009). Biogeophysics: A new frontier in Earth science research. *Reviews of Geophysics*, 47(4), L12505. <https://doi.org/10.1029/2009RG000285>
- Ben Moshe, S., Kessouri, P., Erlich, D., & Furman, A. (2021). Geophysically based analysis of breakthrough curves and ion exchange processes in soil. *Hydrology and Earth System Sciences*, 25(6), 3041–3052. <https://doi.org/10.5194/hess-25-3041-2021>
- Bérubé, C. L., Chouteau, M., Shamsipour, P., Enkin, R. J., & Olivo, G. R. (2017). Bayesian inference of spectral induced polarization parameters for laboratory complex resistivity measurements of rocks and soils. *Computers and Geosciences*, 105, 51–64. <https://doi.org/10.1016/j.cageo.2017.05.001>
- Binley, A., & Slater, L. D. (2020). *Resistivity and induced polarization*. Cambridge University Press. <https://doi.org/10.1017/9781108685955>
- Blagodatskaya, E., & Kuzyakov, Y. (2008). Mechanisms of real and apparent priming effects and their dependence on soil microbial biomass and community structure: Critical review. *Biology and Fertility of Soils*, 45(2), 115–131. <https://doi.org/10.1007/s00374-008-0334-y>
- Camargo, J. A., & Alonso, A. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environment International*, 32(6), 831–849. <https://doi.org/10.1016/j.envint.2006.05.002>
- Che-Alota, V., Atekwana, E. A., Atekwana, E. A., Sauck, W. A., & Werkema, D. D. (2009). Temporal geophysical signatures from contaminant-mass remediation. *Geophysics*, 74(4), B113–B123. <https://doi.org/10.1190/1.3139769>
- Cole, K. S., & Cole, R. H. (1941). Dispersion and absorption in dielectrics I. Alternating current characteristics. *The Journal of Chemical Physics*, 9(4), 341–351. <https://doi.org/10.1063/1.1750906>
- Coleman, T. F., & Li, Y. (1996). An interior trust region approach for nonlinear minimization subject to bounds. *SIAM Journal on Optimization*, 6(2), 418–445. <https://doi.org/10.1137/0806023>
- Critchley, K., Rudolph, D. L., Devlin, J. F., & Schilling, P. C. (2014). Stimulating in situ denitrification in an aerobic, highly permeable municipal drinking water aquifer. *Journal of Contaminant Hydrology*, 171, 66–80. <https://doi.org/10.1016/j.jconhyd.2014.10.008>
- Dahlin, T., Leroux, V., & Nissen, J. (2002). Measuring techniques in induced polarisation imaging. *Journal of Applied Geophysics*, 50(3), 279–298. [https://doi.org/10.1016/S0926-9851\(02\)00148-9](https://doi.org/10.1016/S0926-9851(02)00148-9)
- Davis, C. A., Atekwana, E. A., Atekwana, E. A., Slater, L. D., Rossbach, S., & Mormile, M. R. (2006). Microbial growth and biofilm formation in geologic media is detected with complex conductivity measurements. *Geophysical Research Letters*, 33(18), L18403. <https://doi.org/10.1029/2006GL027312>
- Fiandaca, G., Madsen, L. M., & Maurya, P. K. (2018). Re-parameterisations of the Cole–Cole model for improved spectral inversion of induced polarization data. *Near Surface Geophysics*, 16(4), 385–399. <https://doi.org/10.3997/1873-0604.2017065>
- Gierczak, R. F. D., Devlin, J. F., & Rudolph, D. L. (2007). Field test of a cross-injection scheme for stimulating in situ denitrification near a municipal water supply well. *Journal of Contaminant Hydrology*, 89(1–2), 48–70. <https://doi.org/10.1016/j.jconhyd.2006.08.001>

- Green, C. T., Puckett, L. J., Böhlke, J. K., Bekins, B. A., Phillips, S. P., Kauffman, L. J., et al. (2008). Limited occurrence of denitrification in four shallow aquifers in agricultural areas of the United States. *Journal of Environmental Quality*, 37(3), 994–1009. <https://doi.org/10.2134/jeq2006.0419>
- Griebler, C., & Avramov, M. (2015). Groundwater ecosystem services: A review. *Freshwater Science*, 34(1), 355–367. <https://doi.org/10.1086/679903>
- Griebler, C., & Lueders, T. (2009). Microbial biodiversity in groundwater ecosystems. *Freshwater Biology*, 54(4), 649–677. <https://doi.org/10.1111/j.1365-2427.2008.02013.x>
- Groffman, P. M., Altabet, M. A., Böhlke, J. K., Butterbach-Bahl, K., David, M. B., Firestone, M. K., et al. (2006). Methods for measuring denitrification: Diverse approaches to a difficult problem. *Ecological Applications*, 16(6), 2091–2122. [https://doi.org/10.1890/1051-0761\(2006\)016\[2091:MFMDDA\]2.0.CO;2](https://doi.org/10.1890/1051-0761(2006)016[2091:MFMDDA]2.0.CO;2)
- Hao, N., Moysey, S. M. J., Powell, B. A., & Ntarlagiannis, D. (2015). Evaluation of surface sorption processes using spectral induced polarization and a (22)Na tracer. *Environmental Science & Technology*, 49(16), 9866–9873. <https://doi.org/10.1021/acs.est.5b01327>
- Joo, H.-W., Kwon, T.-H., Lee, S.-R., & Wu, Y. (2021). Relaxation behavior in low-frequency complex conductivity of sands caused by bacterial growth and biofilm formation by *Shewanella oneidensis* under a high-salinity condition. *Geophysics*, 86(6), B389–B400. <https://doi.org/10.1190/GEO2020-0213.1>
- Jougnot, D., Ghorbani, A., Revil, A., Leroy, P., & Cosenza, P. (2010). Spectral induced polarization of partially saturated clay-rocks: A mechanistic approach. *Geophysical Journal International*, 180(1), 210–224. <https://doi.org/10.1111/j.1365-246X.2009.04426.x>
- Katona, T., Gilfedder, B. S., Frei, S., Bücker, M., & Flores Orozco, A. (2021). High-resolution induced polarization imaging of biogeochemical carbon-turnover hot spots in a peatland. *Biogeosciences*, 18(13), 4039–4058. <https://doi.org/10.5194/bg-18-4039-2021>
- Kessouri, P., Furman, A., Huisman, J. A., Martin, T., Mellage, A., Ntarlagiannis, D., et al. (2019). Induced polarization applied to biogeophysics: Recent advances and future prospects. *Near Surface Geophysics*, 17(6), 595–621. <https://doi.org/10.1002/nsg.12072>
- Kimak, C., Ntarlagiannis, D., Slater, L. D., Atekwana, E. A., Beaver, C. L., Rossbach, S., et al. (2019). Geophysical monitoring of hydrocarbon biodegradation in highly conductive environments. *Journal of Geophysical Research: Biogeosciences*, 124(2), 353–366. <https://doi.org/10.1029/2018JG004561>
- Klingler, S., Cirpka, O. A., Werban, U., Leven, C., & Dietrich, P. (2020). Direct-push color logging images spatial heterogeneity of organic carbon in floodplain sediments. *Journal of Geophysical Research: Biogeosciences*, 125(12), e2020JG005887. <https://doi.org/10.1029/2020JG005887>
- Konings, W. N., Albers, S.-V., Koning, S., & Driessen, A. J. (2002). The cell membrane plays a crucial role in survival of bacteria and archaea in extreme environments. *Antonie van Leeuwenhoek*, 81(1–4), 61–72. <https://doi.org/10.1023/A:1020573408652>
- Kuypers, M. M. M., Marchant, H. K., & Kartal, B. (2018). The microbial nitrogen-cycling network. *Nature Reviews Microbiology*, 16(5), 263–276. <https://doi.org/10.1038/nrmicro.2018.9>
- Leckie, S. E., Prescott, C. E., Grayston, S. J., Neufeld, J. D., & Mohn, W. W. (2004). Comparison of chloroform fumigation-extraction, phospholipid fatty acid, and DNA methods to determine microbial biomass in forest humus. *Soil Biology and Biochemistry*, 36(3), 529–532. <https://doi.org/10.1016/j.soilbio.2003.10.014>
- Lennon, J. T., & Jones, S. E. (2011). Microbial seed banks: The ecological and evolutionary implications of dormancy. *Nature Reviews Microbiology*, 9(2), 119–130. <https://doi.org/10.1038/nrmicro2504>
- Leroy, P., & Revil, A. (2009). A mechanistic model for the spectral induced polarization of clay materials. *Journal of Geophysical Research*, 114(B10), B10202. <https://doi.org/10.1029/2008JB006114>
- Leroy, P., Revil, A., Kemna, A., Cosenza, P., & Ghorbani, A. (2008). Complex conductivity of water-saturated packs of glass beads. *Journal of Colloid and Interface Science*, 321(1), 103–117. <https://doi.org/10.1016/j.jcis.2007.12.031>
- Lesmes, D. P., & Morgan, F. D. (2001). Dielectric spectroscopy of sedimentary rocks. *Journal of Geophysical Research*, 106(B7), 13329–13346. <https://doi.org/10.1029/2000JB900402>
- Li, L., Sullivan, P. L., Benettin, P., Cirpka, O. A., Bishop, K., Brantley, S. L., et al. (2021). Toward catchment hydro-biogeochemical theories. *WIREs Water*, 8(1), e1495. <https://doi.org/10.1002/wat2.1495>
- Maloney, P. C., Kashket, E. R., & Wilson, T. H. (1974). A protonmotive force drives ATP synthesis in bacteria. *Proceedings of the National Academy of Sciences of the United States of America*, 71(10), 3896–3900. <https://doi.org/10.1073/pnas.71.10.3896>
- Marshall, D. J., & Madden, T. R. (1959). Induced polarization, a study of its causes. *Geophysics*, 24(4), 790–816. <https://doi.org/10.1190/1.1438659>
- Martin, S., Klingler, S., Dietrich, P., Leven, C., & Cirpka, O. A. (2020). Structural controls on the hydrogeological functioning of a floodplain. *Hydrogeology Journal*, 28(8), 2675–2696. <https://doi.org/10.1007/s10040-020-02225-8>
- Mellage, A., Eckert, D., Grösbacher, M., Inan, A. Z., Cirpka, O. A., & Griebler, C. (2015). Dynamics of suspended and attached aerobic toluene degraders in small-scale flow-through sediment systems under growth and starvation conditions. *Environmental Science & Technology*, 49(12), 7161–7169. <https://doi.org/10.1021/es5058538>
- Mellage, A., Holmes, A. B., Linley, S., Vallée, L., Rezanezhad, F., Thomson, N. R., et al. (2018). Sensing coated iron-oxide nanoparticles with spectral induced polarization (SIP): Experiments in natural sand packed flow-through columns. *Environmental Science & Technology*, 52(24), 14256–14265. <https://doi.org/10.1021/acs.est.8b03686>
- Mellage, A., Smeaton, C. M., Furman, A., Atekwana, E. A., Rezanezhad, F., & Van Cappellen, P. (2018). Linking spectral induced polarization (SIP) and subsurface microbial processes: Results from sand column incubation experiments. *Environmental Science & Technology*, 52(4), 2081–2090. <https://doi.org/10.1021/acs.est.7b04420>
- Mellage, A., Smeaton, C. M., Furman, A., Atekwana, E. A., Rezanezhad, F., & Van Cappellen, P. (2019). Bacterial stern layer diffusion: Experimental determination with spectral induced polarization and sensitivity to nitrite toxicity. *Near Surface Geophysics*, 17(6), 623–635. <https://doi.org/10.1002/nsg.12058>
- Mellage, A., Zakai, G., Efrati, B., Pagel, H., & Schwartz, N. (2022). Paraquat sorption- and organic matter-induced modifications of soil spectral induced polarization (SIP) signals. *Geophysical Journal International*, 229(2), 1422–1433. <https://doi.org/10.1093/gji/ggab531>
- Miao, Z., Brusseau, M. L., Carroll, K. C., Carreón-Diazconti, C., & Johnson, B. (2012). Sulfate reduction in groundwater: Characterization and applications for remediation. *Environmental Geochemistry and Health*, 34(4), 539–550. <https://doi.org/10.1007/s10653-011-9423-1>
- Morse, J. W., Arvidson, R. S., & Lüttge, A. (2007). Calcium carbonate formation and dissolution. *Chemical Reviews*, 107(2), 342–381. <https://doi.org/10.1021/cr050358j>
- Ntarlagiannis, D., Doherty, R., & Williams, K. H. (2010). Spectral induced polarization signatures of abiotic FeS precipitation. *Geophysics*, 75(4), F127–F133. <https://doi.org/10.1190/1.3467759>
- Ntarlagiannis, D., Williams, K. H., Slater, L. D., & Hubbard, S. S. (2005). Low-frequency electrical response to microbial induced sulfide precipitation. *Journal of Geophysical Research*, 110(G2), G00G09. <https://doi.org/10.1029/2005JG000024>
- Oldham, C. E., Farrow, D. E., & Peiffer, S. (2013). A generalized Damköhler number for classifying material processing in hydrological systems. *Hydrology and Earth System Sciences*, 17(3), 1133–1148. <https://doi.org/10.5194/hess-17-1133-2013>

- Pelton, W. H., Ward, S. H., Hallof, P. G., Sill, W. R., & Nelson, P. H. (1978). Mineral discrimination and removal of inductive coupling with multifrequency IP. *Geophysics*, 43(3), 588–609. <https://doi.org/10.1190/1.1440839>
- Pinay, G., Peiffer, S., de Dreuz, J.-R., Krause, S., Hannah, D. M., Fleckenstein, J. H., et al. (2015). Upscaling nitrogen removal capacity from local hotspots to low stream orders' drainage basins. *Ecosystems*, 18(6), 1101–1120. <https://doi.org/10.1007/s10021-015-9878-5>
- Poonia, S. R., & Talibudeen, O. (1977). Sodium-calcium exchange equilibria in salt-affected and normal soils. *Journal of Soil Science*, 28(2), 276–288. <https://doi.org/10.1111/j.1365-2389.1977.tb02236.x>
- Poortinga, A. T., Bos, R., Norde, W., & Busscher, H. J. (2002). Electric double layer interactions in bacterial adhesion to surfaces. *Surface Science Reports*, 47(1), 1–32. [https://doi.org/10.1016/S0167-5729\(02\)00032-8](https://doi.org/10.1016/S0167-5729(02)00032-8)
- Rahman, W. A., & Rowell, D. L. (1979). The influence of magnesium in saline and sodic soils: A specific effect or a problem of cation exchange? *Journal of Soil Science*, 30(3), 535–546. <https://doi.org/10.1111/j.1365-2389.1979.tb01007.x>
- Revil, A., Atekwana, E. A., Zhang, C., Jardani, A., & Smith, S. (2012). A new model for the spectral induced polarization signature of bacterial growth in porous media. *Water Resources Research*, 48(9), W09545. <https://doi.org/10.1029/2012WR011965>
- Revil, A., & Florsch, N. (2010). Determination of permeability from spectral induced polarization in granular media. *Geophysical Journal International*, 181(3), 1480–1498. <https://doi.org/10.1111/j.1365-246X.2010.04573.x>
- Rezanezhad, F., Kleimeier, C., Milojevic, T., Liu, H., Weber, T. K. D., Van Cappellen, P., & Lennartz, B. (2017). The role of pore structure on nitrate reduction in peat soil: A physical characterization of pore distribution and solute transport. *Wetlands*, 37(5), 951–960. <https://doi.org/10.1007/s13157-017-0930-4>
- Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W. N., & Bemment, C. D. (2008). Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Research*, 42(16), 4215–4232. <https://doi.org/10.1016/j.watres.2008.07.020>
- Rosier, C. L., Atekwana, E. A., Abdel Aal, G. Z., & Patrauchan, M. A. (2019). Cell concentrations and metabolites enhance the SIP response to biofilm matrix components. *Journal of Applied Geophysics*, 160, 183–194. <https://doi.org/10.1016/j.jappgeo.2018.10.023>
- Sanchis, A., Brown, A. P., Sancho, M., Martínez, G., Sebastián, J. L., Muñoz, S., & Miranda, J. M. (2007). Dielectric characterization of bacterial cells using dielectrophoresis. *Bioelectromagnetics*, 28(5), 393–401. <https://doi.org/10.1002/bem.20317>
- Saneiyani, S., Ntargiannis, D., & Colwell, F. (2020). Complex conductivity signatures of microbial induced calcite precipitation, field and laboratory scales. *Geophysical Journal International*, 224(3), 1811–1824. <https://doi.org/10.1093/gji/ggaa510>
- Saneiyani, S., Ntargiannis, D., Ohan, J., Lee, J., Colwell, F., & Burns, S. (2019). Induced polarization as a monitoring tool for in-situ microbial induced carbonate precipitation (MICP) processes. *Ecological Engineering*, 127, 36–47. <https://doi.org/10.1016/j.ecoleng.2018.11.010>
- Scheidegger, A. E. (1961). General theory of dispersion in porous media. *Journal of Geophysical Research*, 66(10), 3273–3278. <https://doi.org/10.1029/JZ066i010p03273>
- Schwarz, G. (1962). A theory of the low-frequency dielectric dispersion of colloidal particles in electrolyte solution 1,2. *The Journal of Physical Chemistry*, 66(12), 2636–2642. <https://doi.org/10.1021/j100818a067>
- Scott, J., & Barker, R. D. (2003). Determining pore-throat size in Permo-Triassic sandstones from low-frequency electrical spectroscopy. *Geophysical Research Letters*, 30(9), 1450. <https://doi.org/10.1029/2003GL016951>
- Shampine, L. F., & Reichelt, M. W. (1997). The MATLAB ODE suite. *SIAM Journal on Scientific Computing*, 18(1), 1–22. <https://doi.org/10.1137/S1064827594276424>
- Slater, L. D., & Glaser, D. R. (2003). Controls on induced polarization in sandy unconsolidated sediments and application to aquifer characterization. *Geophysics*, 68(5), 1547–1558. <https://doi.org/10.1190/1.1620628>
- Slouka, C., Brunauer, G., Kopp, J., Strahammer, M., Fricke, J., Fleig, J., & Herwig, C. (2017). Low-frequency electrochemical impedance spectroscopy as a monitoring tool for yeast growth in industrial brewing processes. *Chemosensors*, 5(3), 24. <https://doi.org/10.3390/chemosensors5030024>
- Slouka, C., Wurm, D. J., Brunauer, G., Welzl-Wachter, A., Spadiut, O., Fleig, J., & Herwig, C. (2016). A novel application for low frequency electrochemical impedance spectroscopy as an online process monitoring tool for viable cell concentrations. *Sensors*, 16(11), 1900. <https://doi.org/10.3390/s16111900>
- Stolpovsky, K., Martinez-Lavanchy, P., Heipieper, H. J., Van Cappellen, P., & Thullner, M. (2011). Incorporating dormancy in dynamic microbial community models. *Ecological Modelling*, 222(17), 3092–3102. <https://doi.org/10.1016/j.ecolmodel.2011.07.006>
- Störko, A. (2019). Autosip (Version 1.0) (Computer software). Retrieved from <https://github.com/astoriko/autosip>
- Störko, A., Pagel, H., Mellage, A., & Cirpka, O. A. (2021). Does it pay off to explicitly link functional gene expression to denitrification rates in reaction models? *Frontiers in Microbiology*, 12, 684146. <https://doi.org/10.3389/fmicb.2021.684146>
- Störko, A., Pagel, H., Mellage, A., Van Cappellen, P., & Cirpka, O. A. (2022). Denitrification-driven transcription and enzyme production at the river-groundwater interface: Insights from reactive-transport modeling. *Water Resources Research*, 58(8), e2021WR031584. <https://doi.org/10.1029/2021wr031584>
- Strobel, C., Abramov, S., Huisman, J. A., Cirpka, O. A., & Mellage, A. (2022). Electronic appendix to: Spectral induced polarization (SIP) of denitrification-driven microbial activity in column experiments packed with calcareous aquifer sediments [Dataset]. Zenodo. <https://doi.org/10.5281/zenodo.7032328>
- Tamir, G., Shenker, M., Heller, H., Bloom, P. R., Fine, P., & Bar-Tal, A. (2012). Dissolution and Re-crystallization processes of active calcium carbonate in soil developed on tufa. *Soil Science Society of America Journal*, 76(5), 1606–1613. <https://doi.org/10.2136/sssaj2012.0041>
- Tesoriero, A. J., & Puckett, L. J. (2011). O₂ reduction and denitrification rates in shallow aquifers. *Water Resources Research*, 47(12), 12522. <https://doi.org/10.1029/2011wr010471>
- Titov, K., Komarov, V., Tarasov, V., & Levitski, A. (2002). Theoretical and experimental study of time domain-induced polarization in water-saturated sands. *Journal of Applied Geophysics*, 50(4), 417–433. [https://doi.org/10.1016/S0926-9851\(02\)00168-4](https://doi.org/10.1016/S0926-9851(02)00168-4)
- Turick, C. E., Shimpalee, S., Satjaritanun, P., Weidner, J., & Greenway, S. (2019). Convenient non-invasive electrochemical techniques to monitor microbial processes: Current state and perspectives. *Applied Microbiology and Biotechnology*, 103(20), 8327–8338. <https://doi.org/10.1007/s00253-019-10091-y>
- van der Wal, A., Minor, M., Zehnder, A. J., & Lyklema, J. (1997). Conductivity and dielectric dispersion of gram-positive bacterial cells. *Journal of Colloid and Interface Science*, 186(1), 71–79. <https://doi.org/10.1006/jcis.1996.4615>
- Vaudelet, P., Revil, A., Schmutz, M., Franceschi, M., & Bégassat, P. (2011). Induced polarization signatures of cations exhibiting differential sorption behaviors in saturated sands. *Water Resources Research*, 47(2), W02526. <https://doi.org/10.1029/2010WR009310>
- Weller, A., & Slater, L. D. (2019). Permeability estimation from induced polarization: An evaluation of geophysical length scales using an effective hydraulic radius concept. *Near Surface Geophysics*, 17(6), 581–594. <https://doi.org/10.1002/nsg.12071>
- Werth, C. J., Zhang, C., Brusseau, M. L., Oostrom, M., & Baumann, T. (2010). A review of non-invasive imaging methods and applications in contaminant hydrogeology research. *Journal of Contaminant Hydrology*, 113(1–4), 1–24. <https://doi.org/10.1016/j.jconhyd.2010.01.001>

- Williams, K. H., Ntarlagiannis, D., Slater, L. D., Dohnalkova, A., Hubbard, S. S., & Banfield, J. F. (2005). Geophysical imaging of stimulated microbial biomineralization. *Environmental Science & Technology*, 39(19), 7592–7600. <https://doi.org/10.1021/es0504035>
- Zhang, C., Revil, A., Fujita, Y., Munakata-Marr, J., & Redden, G. (2014). Quadrature conductivity: A quantitative indicator of bacterial abundance in porous media. *Geophysics*, 79(6), D363–D375. <https://doi.org/10.1190/geo2014-0107.1>
- Zimmermann, E., Kemna, A., Berwix, J., Glaas, W., Münch, H. M., & Huisman, J. A. (2008). A high-accuracy impedance spectrometer for measuring sediments with low polarizability. *Measurement Science and Technology*, 19(10), 105603. <https://doi.org/10.1088/0957-0233/19/10/105603>

References From the Supporting Information

- Amalfitano, S., & Fazi, S. (2008). Recovery and quantification of bacterial cells associated with streambed sediments. *Journal of Microbiological Methods*, 75(2), 237–243. <https://doi.org/10.1016/j.mimet.2008.06.004>
- Griebler, C., Mindl, B., Slezak, D., & Geiger-Kaiser, M. (2002). Distribution patterns of attached and suspended bacteria in pristine and contaminated shallow aquifers studied with an in situ sediment exposure microcosm. *Aquatic Microbial Ecology*, 28, 117–129. <https://doi.org/10.3354/ame028117>
- Parkhurst, D. L. (1995). *Users guide to PHREEQC: A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations*. U.S. Department of the Interior, U.S. Geological Survey, Earth Science Information Center, Open-File Reports Section (distributor). Retrieved from <https://search.library.wisc.edu/catalog/999778194102121>

A.2. Publication 2

Geophysical Research Letters[®]



RESEARCH LETTER

10.1029/2023GL104630

Key Points:

- Organic matter (OM) with a high cation exchange capacity can dominate the imaginary conductivity response of sediments
- Neglecting OM may bias petro-physical interpretations of spectral induced polarization measurements

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

A. Mella and C. Strobel,
adrian.mella@uni-kassel.de;
cora.strobel@uni-tuebingen.de

Citation:

Strobel, C., Doerrich, M., Stieff, E.-H., Huisman, J. A., Cirpka, O. A., & Mella, A. (2023). Organic matter matters—The imaginary conductivity of sediments rich in solid organic carbon. *Geophysical Research Letters*, 50, e2023GL104630. <https://doi.org/10.1029/2023GL104630>

Received 19 MAY 2023

Accepted 18 NOV 2023

Corrected 2 DEC 2024

This article was corrected on 2 DEC 2024. See the end of the full text for details.

Author Contributions:

Conceptualization: C. Strobel, J. A. Huisman, O. A. Cirpka, A. Mella
Data curation: C. Strobel
Formal analysis: C. Strobel
Investigation: C. Strobel, M. Doerrich, E.-H. Stieff
Methodology: C. Strobel, M. Doerrich, E.-H. Stieff
Resources: O. A. Cirpka, A. Mella
Supervision: J. A. Huisman, O. A. Cirpka, A. Mella
Visualization: C. Strobel
Writing – original draft: C. Strobel
Writing – review & editing: J. A. Huisman, O. A. Cirpka, A. Mella

© 2023. The Authors.

This is an open access article under the terms of the [Creative Commons Attribution License](#), which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Organic Matter Matters—The Imaginary Conductivity of Sediments Rich in Solid Organic Carbon

C. Strobel^{1,2} , M. Doerrich¹, E.-H. Stieff¹, J. A. Huisman³ , O. A. Cirpka¹ , and A. Mella²

¹Department of Geosciences, University of Tübingen, Tübingen, Germany, ²Civil and Environmental Engineering, University of Kassel, Kassel, Germany, ³Institute of Bio- and Geosciences, Forschungszentrum Jülich GmbH, Agrosphere (IBG-3), Jülich, Germany

Abstract Solid organic matter (OM) is a biogeochemically relevant constituent of soils and sediments. It also affects sediments' geophysical properties, but is often overlooked in hydro- and biogeophysical approaches for the characterization of the shallow subsurface. Here, we explore the potential of spectral induced polarization (SIP) to delineate OM-rich zones in the subsurface and provide insights into the mechanisms that drive OM-polarization using measurements on both field cores and artificial OM-sand mixtures. Both, field samples and artificial mixtures showed a linear relationship between the total organic carbon (TOC) content and charge storage (imaginary conductivity). The high cation exchange capacity of OM drives the increase in polarization and can help in delineating potentially microbially active OM-rich zones in cores or field surveys. To avoid misinterpretation of SIP data in unconsolidated media, we strongly suggest quantifying TOC content in sediment samples to accompany the interpretation of field surveys.

Plain Language Summary Soils and sediments are mixtures of minerals, water, air and partly decomposed organic matter (OM) derived from plants and soil organisms. The field of geophysics measures the electrical, seismic, and magnetic properties of soils and sediments and relates them to the minerals to derive images of their composition. The contribution of the organic fraction is largely ignored. We performed experiments that show that the organic-matter fraction can contribute significantly to the electrical signal of sediments. In fact, our data show that we can locate areas of high organic content in soils using the geophysical technique of spectral induced polarization. We performed measurement on sediment profiles from a natural aquifer and lab experiments on mixtures of peat and sand, to derive a relationship between organic content and the charge storage capacity of sediments. Our results show the potential of using geophysics to map out organic content in sediments, and caution the disregard for OM when deriving physical models of sediment using electrical measurements.

1. Introduction

Solid organic matter (OM) plays a crucial role in providing substrates for microorganisms, as well as the retardation and degradation of contaminants in natural porous media (soils and sediments). Understanding its geoelectrical properties is important for hydro- and biogeophysical surveys in OM-containing sediments, because of its ubiquitous presence and heterogeneous distribution. In particular, delineating its distribution in the subsurface may help to identify potential locations of substrate enrichment that can fuel biogeochemical turnover (Flores Orozco et al., 2020; Katona et al., 2021). A growing, yet limited number of studies have shown promising, and often conflicting, evidence that (spectral) induced polarization (SIP) is sensitive to the presence of OM (Katona et al., 2021; Mella et al., 2022; Ponziani et al., 2012; Schwartz & Furman, 2014).

Measurements of SIP are typically expressed as complex conductivity (σ^*) values (Equation 1). The real part (σ') is a function of electrical conduction in the pore fluid (i.e., electrolytic conductivity) and along particle surfaces (i.e., surface conductivity). The imaginary part (σ'') is a function of the polarization of charged surfaces, that is, the charge storage capacity of the sediment (Binley & Slater, 2020; Slater & Glaser, 2003 and references therein).

$$\sigma^* = \sigma' + i \cdot \sigma'' \quad (1)$$

Electrochemical polarization of the electrical double layer (EDL) that surrounds charged surfaces is expected to be the dominating polarization mechanism in unconsolidated sediments (Bücker et al., 2019). However, the polarization mechanisms of OM remain largely unknown (Katona et al., 2021; Mella et al., 2022; Schwartz &

Furman, 2014). Electrochemical polarization models for mineral sediments are based on surface complexation models that estimate the surface conductivity in the Stern and diffuse layers of the EDL (Leroy & Revil, 2009; Leroy et al., 2008; Revil & Skold, 2011). They yield a linear relationship between σ'' and the surface site density, Γ_s [sites m^{-2}], which can be determined from the cation exchange capacity (CEC) [$\text{mmol}_{\text{charge}} \text{g}_{\text{sed}}^{-1}$] and surface area, A_{surf} [$\text{m}^2 \text{g}_{\text{sed}}^{-1}$], using:

$$\Gamma_s = \frac{\text{CEC}}{A_{\text{surf}}} \quad (2)$$

so that the CEC, a comparatively easy to acquire bulk property of sediments, can reliably predict the polarizability of a sediment (Revil et al., 2023).

Here, we quantify the (linear) relationship between CEC and the σ'' of aquifer sediment cores, and over a broad range of OM-content in artificial mixtures of peat and calcite sand. We explore the applicability of EDL-based models for organic surfaces and derive petro-, or rather, *organo*-physical relationships between the total organic carbon (TOC) content and σ'' . We demonstrate that SIP can delineate zones rich in OM, and that even low fractions of OM (TOC <1%) significantly alter the electrical properties of unconsolidated media.

2. Materials and Methods

2.1. SIP Measurements on Field Cores

We extracted two fresh field cores (2.5–8.4 m depth, 51 mm diameter) from a 6–8 m thick confined Tufa aquifer characterized by autochthonous biogenic freshwater carbonates, near Tübingen, southwest Germany. The OM content of the sediments ranges from ~1% TOC to >50% TOC in naturally occurring peat layers. The cores were taken in the area investigated by Klingler et al. (2020) who delineated two extensive peat layers at depths of 4.0–4.2 and 5.55–5.9 m. Further information on the hydrogeological setting can be obtained from Martin et al. (2020). After extraction, the cores were sealed to prevent pore water leakage during transportation.

In the laboratory, we fitted 8 retracted electrodes with 15 cm spacing on the undisturbed 1.2 m liner sections. This allowed us to perform SIP measurements on the sediment without removing it from the liner, helping to maintain the same fully saturated water content as in the field. For this, a hollow 1.5 cm long cylinder (i.d. = 6 mm) was inserted into each hole drilled directly into the liner, and the inner cavity space was filled with agar (15 g L^{-1} in groundwater from the site). Copper electrodes ($d = 5$ mm) were inserted 5 mm into the liquid agar before gelification. We performed SIP measurements in a Wenner- α configuration (two current electrodes with two potential electrodes between them, all with equal spacing) with skip-0, leading to five measurements per core (see Figure S1 in Supporting Information S1 for a schematic illustration and a photograph of the set-up). Each measurement was assigned to the depth at the center between the potential electrodes. Phase shift ($-\varphi$) and impedance magnitude ($|Z|$) were measured at 12°C (corresponding to the site's groundwater temperature) over 45 log-frequency intervals between 0.1 and 1,000 Hz using a reference resistor of 100 Ω and an amplitude of 5 V (Portable SIP Unit, Ontash & Ermac Inc., USA). The results were converted to apparent frequency-dependent complex conductivities using a geometric factor, k [m], determined numerically for the current setup using pyGIMLi (Rücker et al., 2017). To compare the field-core measurements with the measurements on artificial peat-calcite mixtures, we performed a temperature correction of the conductivity magnitude $|\sigma|$ [S m^{-1}] following the procedure of Hayley et al. (2007):

$$|\sigma|^{20^\circ\text{C}} = |\sigma|^{12^\circ\text{C}} + 0.0183 \cdot (20.5^\circ\text{C} - 12^\circ\text{C}) \cdot |\sigma|^{12^\circ\text{C}} \quad (3)$$

We neglected the temperature effect on the φ spectra because the magnitude of φ has been shown to remain relatively constant with temperature, whereas the peak frequency drops with decreasing temperature (Bairlein et al., 2016). This simplification implies that the peak frequency measured in field cores is not directly comparable to that in the artificial peat-calcite mixtures. Following the SIP measurements, we used a splitter to open the cores and homogenized 15–25 cm long sections for TOC, water content/porosity, and CEC determination, following the procedures outlined in Text S1 of Supporting Information S1.

2.2. SIP Measurements of Artificial Peat-Calcite Mixtures

We prepared mixtures of peat, collected from the peat layer in the Tufa aquifer (study site), and calcite (marble) sand to mimic the composition of Tufa, while keeping the electrical conductivity (EC) during the SIP measurements constant. We used the same columns, tubing, pumps, and wet-packing procedure as Strobel, Abramov,

et al. (2023) and followed the approach of Mella et al. (2022) of pore-volume replacement until the EC and pH of the in- and outflow were identical, to ensure chemical equilibrium prior to measurements. (Note: The columns were water saturated once packed and for the duration of the incubation). We used a CaCl_2 solution ($\text{EC} = 1,100 \mu\text{S cm}^{-1}$) as the saturating solution for the column experiments, mimicking the EC of the groundwater measured at wells in close proximity ($<5 \text{ m}$) to the collected cores (aquifer $\text{EC} = 1,100\text{--}1,300 \mu\text{S cm}^{-1}$). The mineral phase of the Tufa is close to pure calcite (see Figure S2 in Supporting Information S1), however, the marble sand lacks the high intra-particle porosity of the Tufa (Strobel, Abramov, et al., 2023). Details on the sediment preparation and column packing, a photograph of the experimental set-up and schematic of the SIP measurements are shown in Text S2 and Figure S3 of Supporting Information S1.

Column SIP measurements were conducted as mentioned above, but with a higher spectral resolution (61 log-frequency intervals between 0.01 and 10,000 Hz) and at room temperature (20.5°C). The geometric factor of the columns was experimentally determined using measurements of the apparent EC of the columns filled with water of known conductivity. We packed triplicate columns for each SOM content (0%, 1%, 3%, 6%, 10%, 20%, 50% and 100% w/w). SIP measurements were performed at three locations using the upper, middle, and lower potential-electrode pairs (see Figure S3 in Supporting Information S1).

We also investigated the effect of porosity, associated with the volume changes caused by SOM addition, on the electrolytic conductivity σ_{el} [S m^{-1}], according to Archie's law (Archie, 1942). The real part of the complex conductivity was separated into an electrolytic contribution and a surface conduction contribution σ'_{surf} by (Vinegar & Waxman, 1984):

$$\sigma' = \sigma_{el} + \sigma'_{\text{surf}} = \sigma_{el} + \frac{\sigma''_{\text{surf}}}{l} \quad (4)$$

where $\sigma''_{\text{surf}} = \sigma''$ and $l = 0.042$, is a proportionality factor between the real and complex part of the surface conductivity as determined by Weller et al. (2013) for a frequency of 1 Hz. After the SIP measurements, the entire sediment of each column was removed and dried at 30°C for 3–7 d to determine the mass and, therefore, volume of water to compute the porosity, before proceeding with the quantification of the total TOC content and CEC (see Text S1 in Supporting Information S1 on details regarding the TOC and CEC quantification). The low temperature was chosen to avoid any compositional changes of the OM prior to CEC and TOC quantification (Enwezor, 1967).

3. Results and Discussion

3.1. Physical and Chemical Properties of the Field Cores

The TOC content, CEC, porosity, σ'' and σ' measured in the Tufa field cores are shown in Figure 1. Both Tufa field cores exhibit similar depth profiles of geochemical and geoelectrical properties. Three depth intervals (2.5–4.0 m, 4.2–5.6 m and 5.9–8.4 m) contain predominantly freshwater carbonates as the main solid component, whereas the two peat layers (4.0–4.2 m and 5.6–5.9 m) consist of 70%–90% OM and 10%–30% carbonates. In the upper Tufa section, where OM was present as mm to cm thick layers, the TOC content was lowest with a minimum of 2.3%. Below the main peat layer at 5.8 m, the Tufa exhibits alternating carbonate deposits and small, often discontinuous mm-thick peat layers between the two cores, yielding a very high cm-scale variability in TOC from less than 5% up to 22%. In the peat layers, the TOC content reaches up to 56%. The variability in the chemical composition with depth is also reflected in the CEC (Figure 1b), as a metric for changing surface charge, and the porosity (Figure 1c), as a proxy for changes in the pore structure and pore network. Both CEC and porosity increase with increasing TOC content. However, the increase in CEC is more pronounced, with an up to 10-fold increase in CEC from the low TOC regions to the peat layers, whereas the porosity increases from a minimum of 68% to up to 83% in the peat.

The complex conductivity measurements also reveal a strong variability of both σ'' (Figure 1d) and σ' (Figure 1e) as a function of depth. In depth intervals with low TOC, σ'' and σ' are also lower, with values of approximately 1.3–2.7 and 400–490 $\mu\text{S cm}^{-1}$, respectively, and high in the peat layers, reaching up to 3.7–5.5 and 470–590 $\mu\text{S cm}^{-1}$, respectively. While both show an increasing trend with increasing TOC content, we observe a 4.2-fold increase of the imaginary part but only a 1.5-fold increase in the real part, highlighting that there are substantial changes in the electrical properties of the sediment surface associated with TOC rather than electrolytic conduction.

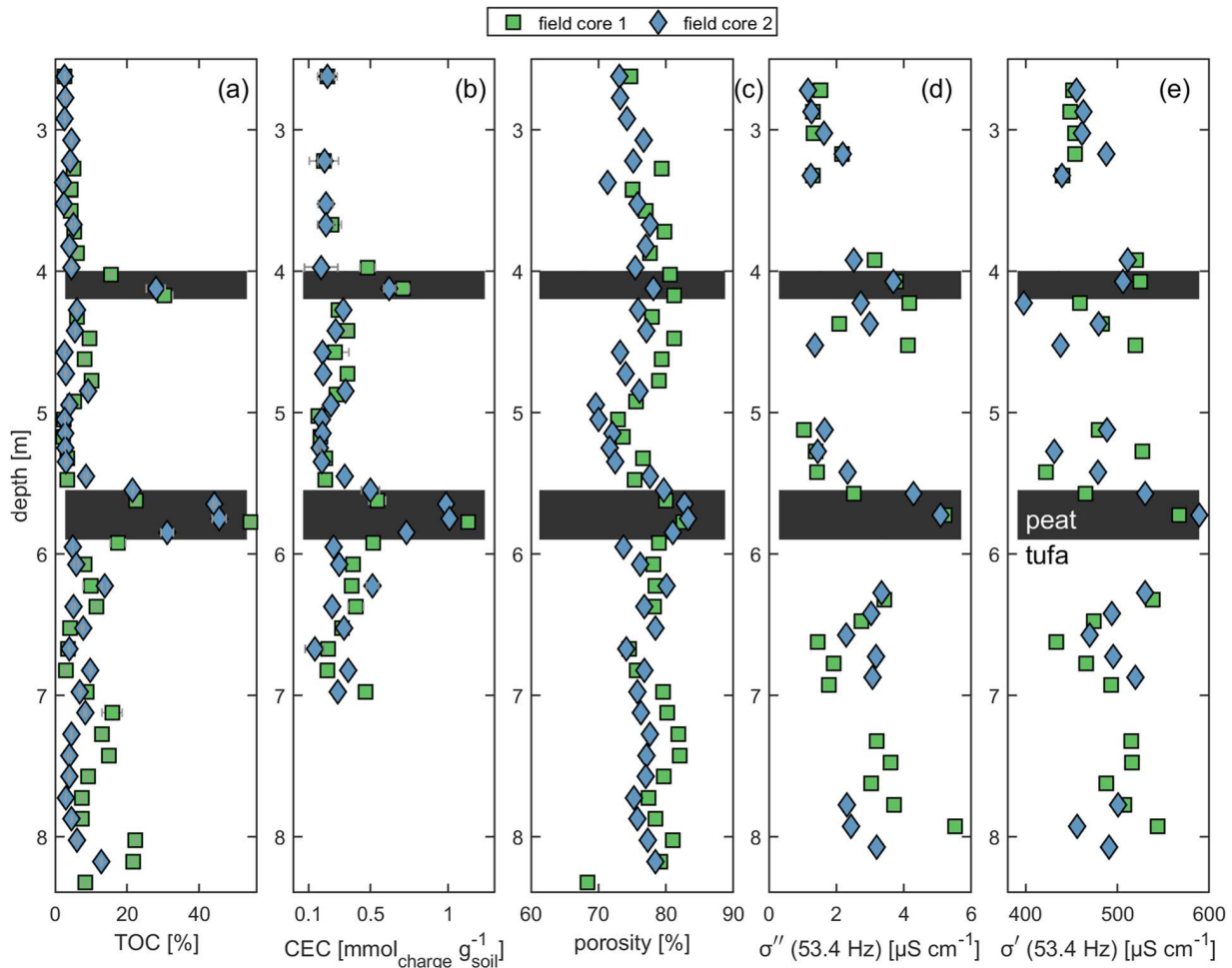


Figure 1. Overview of the field core data, showing the (a) total organic carbon (TOC), (b) cation exchange capacity (CEC), (c) porosity, as well as the (d) imaginary and (e) real part of the complex conductivity at 53.4 Hz depth resolved from 2.5 to 8.4 m depth. Error bars in the TOC and CEC subplots indicate the standard deviation of triplicate measurements and the background colors indicate the sediment characterization as either tufa (white) or peat (dark gray).

The field cores show evidence of a correlation between the TOC content and the imaginary conductivity of the sediment ($R^2 = 0.67$). We believe that the weak correlation is due to the experimental design and the inherent complexity of field samples, yielding a larger spread in the data. Measurement errors resulting from the installation of the electrodes at the core liners (current injection was performed at retracted electrodes) and from partial desaturation of the sediment during the drilling and transport of the cores to the laboratory likely contributed to this spread. Furthermore, we assigned the depth of the SIP measurements to the midpoint of the electrode array. However, SIP signals are sensitive to a volume interval rather than a single point (Mellage et al., 2018). The heterogeneity of the sediment (see Figure S4 in Supporting Information S1 for core photographs), stemming from an irregular sequence of speckled carbonates and peat, likely also led to a slight discrepancy between the SIP measurements and the volume-averaged TOC and CEC. Finally, the, potentially depth-dependent chemistry and EC of the pore water was neither monitored nor held constant for the field cores. (Note: No pore water samples were extracted from the cores to avoid water loss and allow an accurate estimation of porosity). Therefore, we further investigated the relationship between TOC content and complex conductivity using artificial peat-calcite mixtures under more controlled conditions with constant pore water chemistry and conductivity.

3.2. Complex Conductivity of Artificial Peat-Calcite Mixtures and Field Cores

The relationships between complex conductivity (50 Hz) and TOC, CEC, and porosity in the artificial peat-sand mixtures are shown in Figure 2, together with the linear regressions of the real and imaginary conductivities

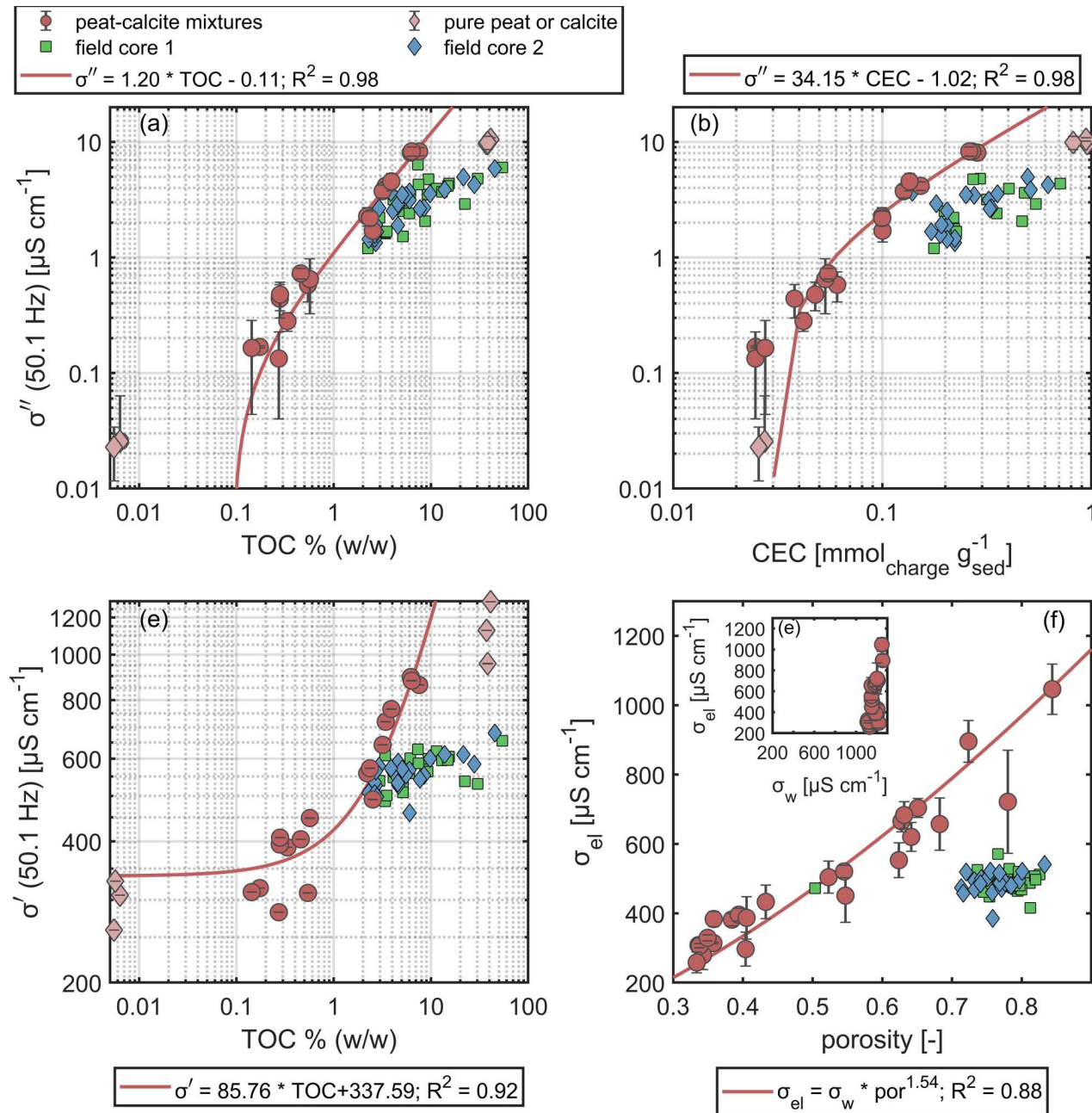


Figure 2. Fitted linear relationships between complex electrical conductivity and selected soil properties: (a) σ'' versus total organic carbon (TOC) content, (b) σ'' versus cation exchange capacity, (c) σ' versus TOC, (d) electrolytic conductivity versus porosity, (e) electrolytic conductivity versus pore water conductivity. Red markers: artificial peat-calcite mixtures; blue/green markers: measurements on field cores from the Tufa aquifer. Error bars for the peat-calcite mixtures show the standard deviation between the three measurements in one column. Note: Pure peat and pure calcite samples (diamond markers) were not considered for fitting the linear relationships for the peat-sand mixtures.

with TOC and CEC (Figures 2a–2c) and Archie's law for the electrolytic conductivity as a function of porosity (Figure 2d). Both σ'' and σ' are presented as average values of all three potential electrode pairs in each triplicate to reduce the variability associated with the packing procedure. The eight different peat-calcite mixtures enabled us to cover a broad range of TOC values spanning over four orders of magnitudes from a trace amount of less than 0.01% in the pure calcite columns to 41% TOC in the pure peat columns. For the linear regressions, we focused on the peat-calcite mixtures, excluding the pure-peat and pure-calcite samples. They lack mineral-OM interactions thereby yielding different relationships between σ'' and σ' and TOC or CEC, likely driven by alternative polarization length scales (see Section 4). In Figure 2a, we show the relationship between the mean σ'' at 50 Hz

and the TOC content of each column. We chose 50 Hz because this is the approximate peak frequency of the peat spectra (spectral data are discussed below), the dominant solid fraction that contributes to polarization. (Note: The relationships in Figure 2 are consistent across the measured frequency range—data not shown). Figure 2a shows a strong positive correlation between σ'' and TOC content. The pore-water composition (i.e., EC) was held constant in the experiment. Therefore, the σ'' -TOC relationship, with a 525-fold increase from $0.02 \mu\text{S cm}^{-1}$ in calcite sand up to $10.5 \mu\text{S cm}^{-1}$ in pure peat, highlights the strong control of OM-polarization, that is, charge storage, on the magnitude of σ'' . While σ' is also positively correlated with the TOC content of the peat-calcite mixtures (red markers in Figure 2c), its much lower relative increase compared to σ'' of a factor 4.4 indicates more substantial changes in the charge-storage properties than in electrolytic and surface conduction of the column fillings with high OM content.

The SIP measurements on the field cores, plotted onto the lab-derived relationships, align very well with the artificial peat-calcite mixtures (green and blue markers in Figure 2), in particular for σ'' and TOC contents between 1% and 10%. At higher TOC contents, the σ'' of the field cores is considerably lower than that of the peat-calcite mixtures. Moreover, the similar magnitude in σ' between the peat-sand mixtures and field cores (Figure 2c) highlights that allowing the 5 mM CaCl_2 packing solution to equilibrate with the peat-sand pack was successful at mimicking the pore-water composition of the Tufa in the laboratory. However, the relationship between the TOC content and σ' seems to follow a different trend in the field cores than in the peat-sand columns, exhibiting a more gradual slope in the field cores. As discussed in Section 3.1, the more controlled laboratory experiment addressed some of the sources of error associated with our measurements on field cores, which we believe are the cause of the differences in slope between peat-sand mixtures and field samples. Moreover, the unknown depth variability in the pore water chemistry of the field cores likely also contributed to the slight offset in σ'' in the field cores compared to the artificial mixtures. We speculate that the OM-calcite association in the Tufa may also be a contributing factor. Peat and calcite sand were only mixed macroscopically in the artificial mixtures but remain separate at the microscopic-level. Conversely, in the aquifer setting of the field cores, OM co-sedimented with the Tufa particles, potentially even stabilizing and binding the calcite nano-crystals (Strobel, Abramov, et al., 2023) that make up the Tufa aggregates. Thus, part of the OM surface in the undisturbed field cores may be “blocked” for polarization, as was already hypothesized by Mellage et al. (2022) and Schwartz and Furman (2014) in the context of organo-mineral complexes.

To gain further insights into the relevant properties of OM that determine its polarization potential, we considered changes in the surface properties (i.e., CEC) and pore structure (i.e., porosity). The addition of OM yielded both an increase in CEC and porosity with increasing TOC content (Figure S5 in Supporting Information S1). Consequently, σ'' is also positively correlated with CEC and porosity (Figure 2b and Figure S5c in Supporting Information S1). The influence of the CEC and a linear relationship between σ'' and CEC is in agreement with existing grain-based polarization models for mineral surfaces and bacteria (e.g., Leroy et al., 2008; Revil et al., 2012).

Interpreting the dependence of the complex EC on changes in the pore structure or porosity is more difficult than that on CEC. Existing models and the joint interpretation of the artificial mixtures and field cores point toward a limited effect of the porosity on σ'' . Porosity affects electrolytic conduction, as described by Archie's law (Archie, 1942). We observed variations in porosity related to OM content. To separate the electrolytic and surface conduction contributions to σ' and to separate the effect of porosity and surface polarization on σ' , we applied Equation 4. We acknowledge that our approach is only an approximation because the frequency-dependence of the proportionality factor l has not been investigated or estimated yet and might be different at 50 Hz compared to 1 Hz (i.e., the frequency it was derived for). Nevertheless, because the resulting electrolytic conductivity follows Archie's law (Text S3 in Supporting Information S1), with a cementation exponent of 1.54 (Figure 2d), in agreement with cementation exponents for unconsolidated sands (Friedman, 2005), we believe that Equation 4 provides a good first-order approximation of the relative contribution of σ_{el} and σ'_{surf} to σ' . Based on this analysis, only about one fifth of the total increase in σ' from calcite sand to pure peat can be attributed to an increase in σ'_{surf} . Moreover, the field-core measurements (blue and green markers in Figure 2d) show a much lower variability in the porosity and almost constant electrolytic conductivity for all measurements, which points toward a significant contribution to the high porosity of the calcite aggregates that make up the Tufa in the field. The marble sand grains in the artificial calcite-peat mixtures lack the secondary porosity of the carbonaceous Tufa thus yielding the wider spread in porosity in our artificial mixtures. This discrepancy may also contribute to the difference in slope of σ' of the field cores and the artificial mixtures (Figure 2c). Nonetheless, the lack of pore-structural changes (or less significant ones) in the field cores coupled to the TOC- σ'' and CEC- σ'' relationships provides strong evidence that porosity plays a minor role in controlling the changes in polarization.

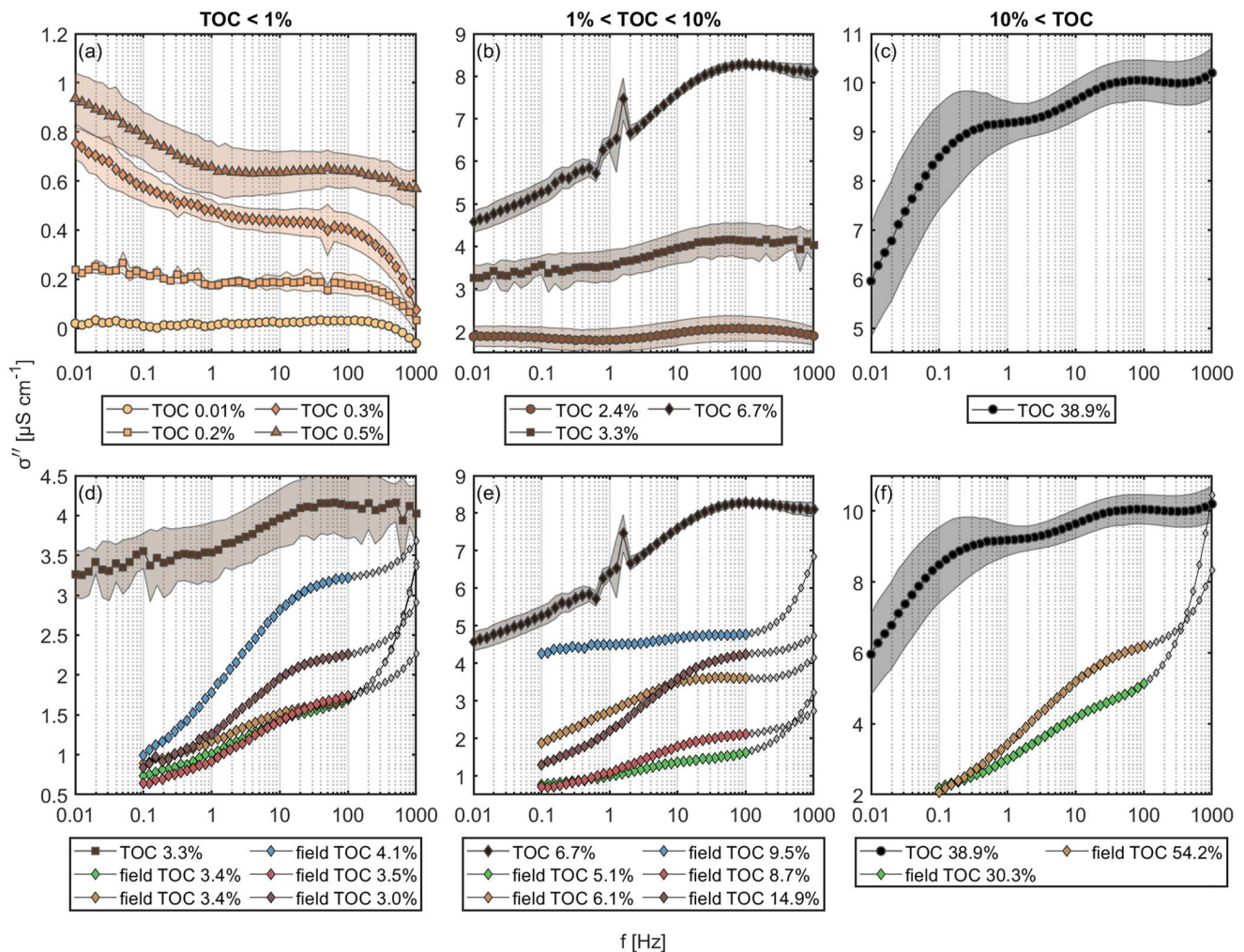


Figure 3. Imaginary conductivity (σ'') spectra of the peat-calcite mixtures. (a): low, (b): medium, (c): high total organic carbon (TOC) contents. The spectra are the averages of triplicates for each treatment, showing their mean value and the standard deviation as a shaded area. In panels (d–f), the spectra of the artificial peat-calcite mixtures are compared to spectra of field core sections with comparable TOC contents. Markers above 100 Hz for field measurements are colored in gray, denoting the lack of confidence in these data related to measurement biases inherent to the electrode array used on the field cores. (Note: the different y-axis scaling for each panel.)

While we cannot fully disentangle the relative effects of pore-structure changes and an increase in surface-site density, existing theory and the excellent agreement between the artificial peat-calcite mixtures and field cores for the relationship between σ'' and CEC (Figure 2b) strongly suggest that our results are driven by polarization stemming from the OM surfaces. Furthermore, the linear relationship between the CEC and σ'' suggests that polarization in our OM-containing sediments is driven by processes analogous to those at mineral surfaces.

4. The Polarization of Organic Matter: σ'' Spectra

In Figures 3a–3c we show the σ'' -spectra separately for low, medium, and high TOC contents (see Figure S6 in Supporting Information S1 for an overview of all σ'' spectra). Apart from a general increase of σ'' at all frequencies, we observe a shift in peak frequency from less than 0.01 Hz for TOC < 1% to 50 Hz in the medium- and high-TOC content mixtures. In addition, the pure peat exhibited a secondary polarization with a peak frequency at about 1.5 Hz. The different frequency-dependent polarization between the mineral-OM mixtures and pure peat highlights a different relationship between σ'' and TOC in pure peat, and justifies its exclusion from our linear regression (Figure 2). The frequency peak is related to the timescale of polarization. Higher frequencies suggest shorter timescales for relaxation and back-diffusion. The time scale is controlled by the chemical properties of the EDL and the length-scale over which ion migration occurs. Thus, for a system with similar chemical proper-

ties, changes in peak frequency suggest a shift in the dominant polarization length scale (e.g., Schwarz (1962), for spherical grains). Assuming that the polarization response is entirely related to the OM and applying the relationship between relaxation time and the polarization length scale (Weller & Slater, 2019) with a constant surface-diffusion coefficient, the shift in peak frequency would correspond to a decrease of the dominant polarization length scale by a factor of about 100. We attribute this shift toward lower polarization length scales to a transition from polarization over single, isolated OM particles in a calcite-sand matrix to the formation of a pore structure network of connected OM particles in which the pore size is now the dominant polarization length scale. In that context, the polarization of pure peat (Figure 3c) would indicate the presence of two main pore sizes. This aligns well with the fact that peat is known to have two dominant pore sizes (dual-porosity) that control the flow of water (Kleimeier et al., 2017; Rezanezhad et al., 2012, 2016), which likely also influence current flow and polarization.

Figures 3d–3f compare the spectra of field cores with those of the artificial mixtures for similar TOC contents. Due to the linear scale of the y-axis, the lower σ'' response in the field cores becomes more prevalent than in Figure 2, but the spectral characteristics are still comparable. (Note: The differences in magnitude between field-core spectra and spectra from the artificial mixtures relate to the differences discussed in Section 3.2, pertaining to the single-frequency relationships that were derived from the spectral responses). Both, field cores and artificial mixtures show an increase in σ'' with increasing frequency and a peak frequency at about 50 Hz. This also holds for the measurements in pure peat, where the field-core spectra lack the secondary peak at about 1.5 Hz (Figure 3f) indicating that it might be an artifact of the repacking of the peat into columns.

5. Conclusions

Solid OM can change the σ'' response of a sediment by several orders of magnitude and should therefore not be neglected in the interpretation of complex conductivity data. Therefore, to prevent data-misinterpretation, the quantification of TOC should be an integral part of the sediment characterization for ground-truthing of (S)IP surveys, in particular, when interpreting data in soils or other OM rich porous media. Our results suggest that the high CEC is the main property of OM that determines its polarization strength.

With a CEC of $1.3 \text{ mmol}_{\text{charge}} \text{ g}_{\text{sed}}^{-1}$, the OM used in this study is comparable to 2:1 clay minerals of very high CEC (e.g., vermiculite with reported CEC values of $1\text{--}1.5 \text{ mmol}_{\text{charge}} \text{ g}_{\text{sed}}^{-1}$) and considerably higher than 1:1 clay minerals such as kaolinite ($0.03\text{--}1.5 \text{ mmol}_{\text{charge}} \text{ g}_{\text{sed}}^{-1}$) or illite ($0.1\text{--}0.4 \text{ mmol}_{\text{charge}} \text{ g}_{\text{sed}}^{-1}$) (Carrol, 1959). Given that the chemical composition of OM is site specific and depends on many factors (e.g., origin of OM, degree of decomposition, pH), the relationship between σ'' and TOC content derived in this work is also specific for the type of OM (peat) used here and should not be directly applied to other systems. A difference in the OM composition and thus also CEC may explain the contrasting results reported by the handful of previous studies that investigated the effect of OM on SIP signals versus this work. Future work on different OM types and mixtures with other polarizing sediment components such as clay minerals could shed light on their relative importance under different environmental conditions. Furthermore, the complex conductivity signal of pure peats will require further investigation to better understand what mechanisms determine the σ'' -signal in peatlands. Given that the CEC of OM is expected to highly depend on pH (Helling et al., 1964), an in-depth characterization of the geochemical conditions in peatlands will be necessary to understand the variability of the complex conductivity signal in purely organic environments.

In addition to highlighting the importance of considering OM in SIP signal interpretation, the findings herein, highlight the relevance of geophysical methods for the characterization of OM-rich soils and peatlands. Such applications are poised to improve our capabilities to monitor carbon cycling at higher spatial and temporal scales in vulnerable, and rapidly changing environments in the era of climate change.

Data Availability Statement

The SIP data, the geochemical data and the data processing and analysis scripts are available at Strobel, Doerrich, et al. (2023).

Acknowledgments

Adrian Mella would like to acknowledge the financial support of the Baden-Württemberg Stiftung received for this project via the Eliteprogramme for Postdocs. The authors gratefully acknowledge Bernice Nisch, Carsten Leven and Christoph Berthold for their support with TOC measurements, field work and pXRD measurements and Thomas Günther for his support with pyGIMLI. Open Access funding enabled and organized by Projekt DEAL.

References

- Archie, G. E. (1942). The electrical resistivity log as an aid in determining some reservoir characteristics. *Transactions of the AIME*, 146(01), 54–62. <https://doi.org/10.2118/942054-g>
- Bairlein, K., Bucker, M., Hördt, A., & Hinze, B. (2016). Temperature dependence of spectral induced polarization data: Experimental results and membrane polarization theory. *Geophysical Journal International*, 205(1), 440–453. <https://doi.org/10.1093/gji/ggw027>
- Binley, A., & Slater, L. (2020). *Resistivity and induced polarization: Theory and applications to the near-surface earth*. Cambridge University Press.
- Bücker, M., Flores Orozco, A., Undorf, S., & Kemna, A. (2019). On the role of stern- and diffuse-layer polarization mechanisms in porous media. *Journal of Geophysical Research: Solid Earth*, 124(6), 5656–5677. <https://doi.org/10.1029/2019JB017679>
- Carroll, D. (1959). Ion exchange in clays and other minerals. *Geological Society of America Bulletin*, 70(6), 749. [https://doi.org/10.1130/0016-7606\(1959\)70\[749:IEICAO\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1959)70[749:IEICAO]2.0.CO;2)
- Enwezor, W. O. (1967). Soil drying and organic matter decomposition. *Plant and Soil*, 26(2), 269–276. <https://doi.org/10.1007/bf01880177>
- Flores Orozco, A., Gallistl, J., Steiner, M., Brandstätter, C., & Fellner, J. (2020). Mapping biogeochemically active zones in landfills with induced polarization imaging: The Heferlbach landfill. *Waste Management*, 107, 121–132. <https://doi.org/10.1016/j.wasman.2020.04.001>
- Friedman, S. P. (2005). Soil properties influencing apparent electrical conductivity: A review. *Computers and Electronics in Agriculture*, 46(1–3), 45–70. <https://doi.org/10.1016/j.compag.2004.11.001>
- Hayley, K., Bentley, L. R., Gharibi, M., & Nightingale, M. (2007). Low temperature dependence of electrical resistivity: Implications for near surface geophysical monitoring. *Geophysical Research Letters*, 34(18), L18402. <https://doi.org/10.1029/2007GL031124>
- Helling, C. S., Chesters, G., & Corey, R. B. (1964). Contribution of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solution. *Soil Science Society of America Journal*, 28(4), 517–520. <https://doi.org/10.2136/sssaj1964.03615995002800040020x>
- Katona, T., Gilfedder, B. S., Frei, S., Bucker, M., & Flores Orozco, A. (2021). High-resolution induced polarization imaging of biogeochemical carbon-turnover hot spots in a peatland. *Biogeosciences*, 18(13), 4039–4058. <https://doi.org/10.5194/bg-18-4039-2021>
- Kleimeier, C., Rezaeezad, F., van Cappellen, P., & Lennartz, B. (2017). Influence of pore structure on solute transport in degraded and undegraded fen peat soils. *Mires Peat*, 19(18), 1–9.
- Klingler, S., Cirpka, O. A., Werban, U., Leven, C., & Dietrich, P. (2020). Direct-Push color logging images spatial heterogeneity of organic carbon in floodplain sediments. *Journal of Geophysical Research: Biogeosciences*, 125(12), e2020JG005887. <https://doi.org/10.1029/2020JG005887>
- Leroy, P., & Revil, A. (2009). A mechanistic model for the spectral induced polarization of clay materials. *Journal of Geophysical Research*, 114(B10), B10202. <https://doi.org/10.1029/2008JB006114>
- Leroy, P., Revil, A., Kemna, A., Cosenza, P., & Ghorbani, A. (2008). Complex conductivity of water-saturated packs of glass beads. *Journal of Colloid and Interface Science*, 321(1), 103–117. <https://doi.org/10.1016/j.jcis.2007.12.031>
- Martin, S., Klingler, S., Dietrich, P., Leven, C., & Cirpka, O. A. (2020). Structural controls on the hydrogeological functioning of a floodplain. *Hydrogeology Journal*, 28(8), 2675–2696. <https://doi.org/10.1007/s10040-020-02225-8>
- Mella, A., Holmes, A. B., Linley, S., Vallée, L., Rezaeezad, F., Thomson, N. R., et al. (2018). Sensing coated iron-oxide nanoparticles with spectral induced polarization (SIP): Experiments in natural sand packed flow-through columns. *Environmental Science & Technology*, 52(24), 14256–14265. <https://doi.org/10.1021/acs.est.8b03686>
- Mella, A., Zakai, G., Efrati, B., Pagel, H., & Schwartz, N. (2022). Paraquat sorption- and organic matter-induced modifications of soil spectral induced polarization (SIP) signals. *Geophysical Journal International*, 229(2), 1422–1433. <https://doi.org/10.1093/gji/ggab531>
- Ponziani, M., Slob, E. C., Vanhala, H., & Ngan-Tillard, D. (2012). Influence of physical and chemical properties on the low-frequency complex conductivity of peat. *Near Surface Geophysics*, 10(6), 491–501. <https://doi.org/10.3997/1873-0604.20110737>
- Revil, A., Atekwana, E. A., Zhang, C., Jardani, A., & Smith, S. (2012). A new model for the spectral induced polarization signature of bacterial growth in porous media. *Water Resources Research*, 48(9). <https://doi.org/10.1029/2012WR011965>
- Revil, A., Ghorbani, A., Jougnot, D., & Yven, B. (2023). Induced polarization of clay-rich materials—Part I: The effect of desiccation. *Geophysics*, 88(4), 1–57. <https://doi.org/10.1190/geo2022-0510.1>
- Revil, A., & Skold, M. (2011). Salinity dependence of spectral induced polarization in sands and sandstones. *Geophysical Journal International*, 187(2), 813–824. <https://doi.org/10.1111/j.1365-246X.2011.05181.x>
- Rezaeezad, F., Price, J. S., & Craig, J. R. (2012). The effects of dual porosity on transport and retardation in peat: A laboratory experiment. *Canadian Journal of Soil Science*, 92(5), 723–732. <https://doi.org/10.4141/CJSS2011-050>
- Rezaeezad, F., Price, J. S., Quinton, W. L., Lennartz, B., Milojevic, T., & Van Cappellen, P. (2016). Structure of peat soils and implications for water storage, flow and solute transport: A review update for geochemists. *Chemical Geology*, 429, 75–84. <https://doi.org/10.1016/j.chemgeo.2016.03.010>
- Rücker, C., Günther, T., & Wagner, F. M. (2017). pyGIMLI: An open-source library for modelling and inversion in geophysics. *Computers & Geosciences*, 109, 106–123. <https://doi.org/10.1016/j.cageo.2017.07.011>
- Schwartz, N., & Furman, A. (2014). On the spectral induced polarization signature of soil organic matter. *Geophysical Journal International*, 200(1), 589–595. <https://doi.org/10.1093/gji/ggu410>
- Schwarz, G. (1962). A theory of the low-frequency dielectric dispersion of colloidal particles in electrolyte solution. *The Journal of Physical Chemistry*, 66(12), 2636–2642. <https://doi.org/10.1021/j100818a067>
- Slater, L. D., & Glaser, D. R. (2003). Controls on induced polarization in sandy unconsolidated sediments and application to aquifer characterization. *Geophysics*, 68(5), 1547–1558. <https://doi.org/10.1190/1.1620628>
- Strobel, C., Abramov, S., Huisman, J. A., Cirpka, O. A., & Mella, A. (2023). Spectral induced polarization (SIP) of denitrification-driven microbial activity in column experiments packed with calcareous aquifer sediments. *Journal of Geophysical Research: Biogeosciences*, 128(1), e2022JG007190. <https://doi.org/10.1029/2022JG007190>
- Strobel, C., Doerrich, M., Stieff, E.-H., Huisman, J. A., Cirpka, O. A., & Mella, A. (2023). Electronic appendix to: Organic matter matters—The imaginary conductivity of sediments rich in solid organic carbon [Dataset]. <https://doi.org/10.5281/zenodo.14033179>
- Vinegar, H. J., & Waxman, M. H. (1984). Induced polarization of shaly sands. *Geophysics*, 49(8), 1267–1287. <https://doi.org/10.1190/1.1441755>
- Weller, A., Slater, L., & Nordsiek, S. (2013). On the relationship between induced polarization and surface conductivity: Implications for petrophysical interpretation of electrical measurements. *Geophysics*, 78(5), D315–D325. <https://doi.org/10.1190/geo2013-0076.1>
- Weller, A., & Slater, L. D. (2019). Permeability estimation from induced polarization: An evaluation of geophysical length scales using an effective hydraulic radius concept. *Near Surface Geophysics*, 17(6), 581–594. <https://doi.org/10.1002/nsg.12071>

References From the Supporting Information

- Rühlmann, J., Körschens, M., & Graefe, J. (2006). A new approach to calculate the particle density of soils considering properties of the soil organic matter and the mineral matrix. *Geoderma*, 130(3), 272–283. <https://doi.org/10.1016/j.geoderma.2005.01.024>
- Sumner, M. E., & Miller, W. P. (1996). Cation exchange capacity and exchange coefficients. In D. L. Sparks, A. L. Page, P. A. Helmke, R. H. Loeppert, P. N. Soltanpour, M. A. Tabatabai, et al. (Eds.), *Methods of soil analysis* (pp. 1201–1229). Soil Science Society of America, American Society of Agronomy (SSSA Book Series).

Erratum

The originally published version of this article contained an error in how the authors derived the relationship between imaginary conductivity (σ'') and solid organic carbon content (as TOC). In particular, the authors fitted a linear model in log-log space, which corresponds to a power-law relationship and not a linear relationship in linear space, as was erroneously reported in the original article. Therefore, they revisited their analysis and fit a linear model in linear space to provide a more quantitatively sound TOC- σ'' relationship. Figure 1 now shows a comparison of the previous power-law and the new linear relationship both in a linear-linear and a log-log plot (upper and lower row, respectively). In line with the authors' interpretation of contrasting polarization length scales (Section 4) in pure peat and mixtures of peat and calcite-sand, the authors have omitted the pure-peat and pure-calcite samples and limited the revised analysis to mixed mineral-OM samples. The following text should be added after the third sentence of the first paragraph of Section 3.2: "For the linear regressions, we focused on the peat-calcite mixtures, excluding the pure-peat and pure-calcite samples. They lack mineral-OM interactions thereby yielding different relationships between σ'' and σ' and TOC or CEC, likely driven by alternative polarization length scales (see Section 4)." The following text should be included after the third sentence of Section 4: "The different frequency-dependent polarization between the mineral-OM mixtures and pure peat highlights a different relationship between σ'' and TOC in pure peat and justifies its exclusion from our linear regression (Figure 2)." This is in full agreement with the original conclusions, where the authors discussed that controls on polarization in pure peat might vary from sediment mixtures: "Furthermore, the complex conductivity signal of pure peats will require further investigation to better understand what mechanisms determine the σ'' -signal in peatlands. Given that the CEC of OM is expected to highly depend on pH (Helling et al., 1964), an in-depth characterization of the geochemical conditions in peatlands will be necessary to understand the variability of the complex conductivity signal in purely organic environments." Finally, The caption of Figure 2 also needs to be changed as follows: "Figure 2. Fitted linear relationships between complex electrical conductivity and selected soil properties: (a) σ'' versus total organic carbon (TOC) content, (b) σ'' versus cation exchange capacity, (c) σ' versus TOC, (d) electrolytic conductivity versus porosity, (e) electrolytic conductivity versus pore water conductivity. Red markers: artificial peat-calcite mixtures; blue/green markers: measurements on field cores from the Tufa aquifer. Error bars for the peat-calcite mixtures show the standard deviation between the three measurements in one column. Note: Pure peat and pure calcite samples (diamond markers) were not considered for fitting the linear relationships for the peat-sand mixtures." The errors have been corrected, and this may be considered the authoritative version of record.

A.3. Publication 3



Are we there yet? A critical experimental assessment of the application of induced polarization for monitoring geochemical processes

C. Strobel^{1,2*}, A. Störiko³, O.A. Cirpka¹ and A. Melling^{2, **}

¹Department of Geosciences, University of Tübingen, Tübingen, Germany

²Civil and Environmental Engineering, University of Kassel, Kassel, Germany

³Department of Water Management, Delft University of Technology, Delft, Netherlands

*Corresponding author: Cora Strobel, University of Tübingen, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany; (cora.strobel@uni-tuebingen.de)

** Secondary corresponding author: Adrian Melling, adrian.melling@uni-kassel.de

Key Points:

- The (ad)sorption strength of the exchanging cation determines its effect on imaginary conductivity during cation exchange.
- We propose separating the effect of ion exchange and salinity changes on the imaginary conductivity using a transport model.
- The imaginary conductivity as a proxy for sorbed concentrations cannot replace geochemical samples.

Abstract

Spectral induced polarization (SIP) can provide valuable information about (bio)geochemical processes taking place in the poorly accessible subsurface. The method is sensitive to reactions that alter the solid-water interface. Here, we critically evaluate the effectiveness of SIP to monitor geochemical processes by focusing on a model-supported analysis of cation exchange dynamics in sediments containing organic matter. Organic matter is a crucial substrate for contaminant immobilization that exhibits a strong SIP response. We compare the SIP response of columns during the injection of cations (Na^+ , Ca^{2+} and Zn^{2+}) with different sorption strengths. We assess whether a change in surface ion mobility due to cation exchange is reflected by an increasing (Na^+ , high surface mobility) or decreasing (Zn^{2+} , low surface mobility) imaginary conductivity. Our work demonstrates how we can qualitatively monitor reactive solute fronts using (S)IP, thus, helping to target sampling events. Furthermore, we explore the quantitative value of SIP datasets in constraining reactive transport models. We use the imaginary conductivity as a proxy for sorbed concentrations by separating the contributions of ion exchange and bulk electrical conductivity to changes in imaginary conductivity. By integrating a Bayesian parameter-estimation scheme, we test whether the use of SIP can replace geochemical sampling and improve reaction-parameter estimates. While inverting SIP-data alone does not yield better results than breakthrough samples, their integration reduces the uncertainty of some parameters, highlighting their potential value. Finally, we discuss opportunities and limitations for reaction monitoring using SIP and provide an outlook for its successful application by non-geophysicists.

Plain-Language Summary

Understanding and monitoring geochemical processes in the subsurface is crucial for managing environmental challenges. However, the subsurface is difficult to access, and traditional sampling methods can be time-consuming and invasive. Spectral induced polarization (SIP) offers a promising alternative by providing indirect but detailed insights into these processes. It can detect changes in the electrical properties of sediment particles on which many critical reactions occur. This study investigates the potential of SIP to monitor the adsorption dynamics of cations as they flow through sediments containing organic matter. Organic matter is key for the immobilization of contaminants. By exploring how different cations (sodium, calcium and

zinc) interact with organic matter and alter SIP signals, this research aims to assess SIP's ability to track reactive zones and enhance our understanding of geochemical reactions. We also explore whether SIP could replace traditional sampling methods and improve the accuracy of models used to predict contaminant transport in groundwater. Combining SIP data with traditional sampling helps to improve the accuracy of parameter predictions, showing SIP's potential as a complementary tool for environmental monitoring. Finally, we discuss how SIP could be more widely applied, even by non-specialists, while acknowledging its current limitations and areas for further development.

1 Introduction

Reactive processes in the subsurface are difficult to locate, identify and are very resource-intensive to monitor over time. Yet, they are key to understanding the fate of contaminants in the environment. Sorption on organic matter (OM) is of particular importance for contaminant transport in soils and sediments (Albers et al., 2009; Huang et al., 2003; Lair et al., 2007). The complexity of the OM composition and the lack of information on the concentrations in the sorbing phase (unless the solid phase is sacrificially sampled) often hamper the interpretation of column and field data. Reactive-transport models (RTMs) provide an approach to interpret experiments despite the lack of data as they add theoretical knowledge of the reactive processes to the scarce datasets. They are thus a versatile tool to quantitatively bridge the gap between point measurements, validate the process comprehension, and predict the future behavior of the system under changing conditions (Li et al., 2021). Nevertheless, the lack of information on the solid-phase concentrations can impede the accurate determination of sorption parameters that are required to reliably upscale or extrapolate the findings of small-scale experiments.

The research fields of hydro- and bio-geophysics are evolving to complement traditional monitoring and modeling approaches with higher spatiotemporal resolution, potentially yielding deeper understanding of reactive processes in the hydrosphere (Atekwana & Slater, 2009; Kessouri et al., 2019). Especially the method of (spectral) induced polarization (SIP) has

81 been applied to monitor various reactions at different scales. Examples include organic-
82 contaminant sorption (Ben Moshe & Furman, 2022; Mellage, Zakai, et al., 2022), heavy-metal
83 remediation (Bate et al., 2023; Flores Orozco et al., 2013), microbially-mediated reactions
84 (Mellage et al., 2018; Saneiyan, 2019; Strobel, Abramov, et al., 2023; Zhang et al., 2014), and
85 plant root growth (Tsukanov & Schwartz, 2020; Weigand & Kemna, 2019). The advantage of SIP
86 lies in its sensitivity to surface-related reactions, the non-invasiveness of the measurements,
87 and the high temporal resolution combined with fast data acquisition. The potential of SIP lies
88 therefore not only in complementing geochemical sampling of the pore water with information
89 on the solid phase, but also in serving as a non-invasive, in-line monitoring tool. However, the
90 latter requires that the processing and interpretation of the acquired SIP data is fast,
91 straightforward, and independent of the geochemical sampling that often takes longer to be
92 processed.

93 SIP is an active geoelectrical method in which an alternating current with defined frequency in
94 the mHz to kHz range is injected into the sample through two current electrodes and the
95 resulting impedance magnitude and phase shift are recorded between a second pair of
96 potential electrodes (Binley & Slater, 2020). Within a single data-acquisition cycle, the
97 frequency is tuned to achieve the response over an entire frequency range. The material
98 property that is obtained from the raw measurements is typically expressed as a complex-
99 valued electrical conductivity σ^* (S m^{-1}), in which the real part, σ' , mainly depends on the
100 electrical conduction through the pore fluid and along the grain-fluid interface (Slater & Glaser,
101 2003). The imaginary conductivity, σ'' , is much smaller in magnitude than σ' and reflects
102 electrical charge storage or surface polarization of the solid matrix. It also shows a stronger
103 frequency dependence than σ' , that can provide additional information on the length scale
104 (distribution) of polarization (Schwarz, 1962). In the absence of metallic particles and within the
105 low-frequency range (mHz to kHz), charge storage is controlled by electrochemical polarization
106 of the electrical double layer (EDL). The EDL surrounds charged particles and essentially
107 depends on the surface charge, the bulk fluid composition as well as the salinity and the
108 chemical and electrostatic attraction between dissolved ions and the solid's surface. Under an
109 applied electrical field, ions in the EDL and the corresponding counter ions in the bulk fluid

migrate in response to the external field, causing the polarization around the particles, which alternates if an alternating current is injected. A key parameter that determines the magnitude of electrochemical polarization is the mobility of the counter ions in the EDL during the application of the electric field (Bücker et al., 2019; Leroy et al., 2008; Schwarz, 1962). The mobility of the ions in the EDL depends on their binding strength (both electrostatic and complexation) to the surface. Thus, $\sigma^{\wedge\prime\prime}$ is sensitive to reactions that alter the surface properties or the composition of the EDL, such as cation exchange and other sorption and sorption-like processes (e.g., precipitation and dissolution). Several studies have investigated the effect of different cations on the $\sigma^{\prime\prime}$ signal of mineral sediments that supported the model-based assumption of ion mobility as the controlling factor when comparing the electrochemical polarization of different cations (e.g. Ben Moshe et al. (2021), Hao et al. (2015), and Vaudelet et al. (2011)). Ben Moshe et al. 2021 investigated the suitability of SIP as a monitoring tool in breakthrough-curve analysis under cation exchange conditions in mineral soils. They showed that the real part $\sigma^{\prime}$ can serve as a proxy for conservative transport but were not successful in explaining the dynamics of $\sigma^{\prime\prime}$ during cation exchange or combining them with a reactive-transport model.

SIP surveys have been shown to be sensitive to the presence of solid (i.e. particulate) organic matter (OM) in sediments, with the signal strength of SIP being proportional to the cation exchange capacity (CEC) of OM (Strobel, Doerrich, et al., 2023). However, it is still up for debate whether electrochemical polarization in OM is similar to that at mineral surfaces or whether other factors such as the 3D-structure of OM and organo-mineral complexes yield different polarization mechanisms than those on inorganic minerals (Katona et al., 2021; Mellage, Zakai, et al., 2022; Schwartz & Furman, 2014). Measurements of $\sigma^{\wedge\prime\prime}$ are inherently non-selective and depend on a multitude of factors that are often coupled, integrating parallel contributions from different components of a porous medium. One major difficulty is therefore to distinguish between parallel signal contributions when interpreting $\sigma^{\prime\prime}$ changes. In particular, the electrical conductivity of the pore fluid (EC) often changes when investigating dynamic systems. It is often not feasible nor realistic to keep the EC constant during an experiment. Because the bulk fluid composition and EC can exert a significant control on $\sigma^{\prime\prime}$ (Weller et al. 2011), changes in EC can

mask σ'' variations that are due to a difference in the EDL composition, hampering the interpretation of target processes from σ'' signals (Mellage, Dörrich, et al., 2022).

In this study we focus on cation-exchange reactions on OM. We compare the SIP response during the injection of a monovalent cation (Na^+) and two divalent cations with different surface complexation strengths (Ca^{2+} and Zn^{2+}) into columns filled with a mixture of calcite sand and peat, and initially been loaded with Ca^{2+} -dominated pore water. With this work we want to test the following hypotheses:

(1) Our understanding of surface polarization that was originally developed for mineral surfaces can also explain polarization on OM. Hence, a change in ion mobility on the surface is reflected in an increasing (e.g., via Na^+) or decreasing (e.g., via Zn^{2+}) imaginary conductivity.

(2) We can qualitatively interpret the SIP data in the absence of a reactive-transport model or geochemical data to gain insights into the reaction dynamics. The breakthrough of the injected cation is distinguishable from the breakthrough of the conservatively behaving anion.

(3) SIP measurements can be incorporated into a transport model accounting for competitive sorption to constrain the sorbing-phase concentration of the injected (or replaced) cation, thus improving model quality.

Finally, we provide an outlook on what is needed to successfully monitor reactions using SIP by non-geophysicists to unravel its potential in providing a glimpse into the “black box” of the subsurface without soil sampling.

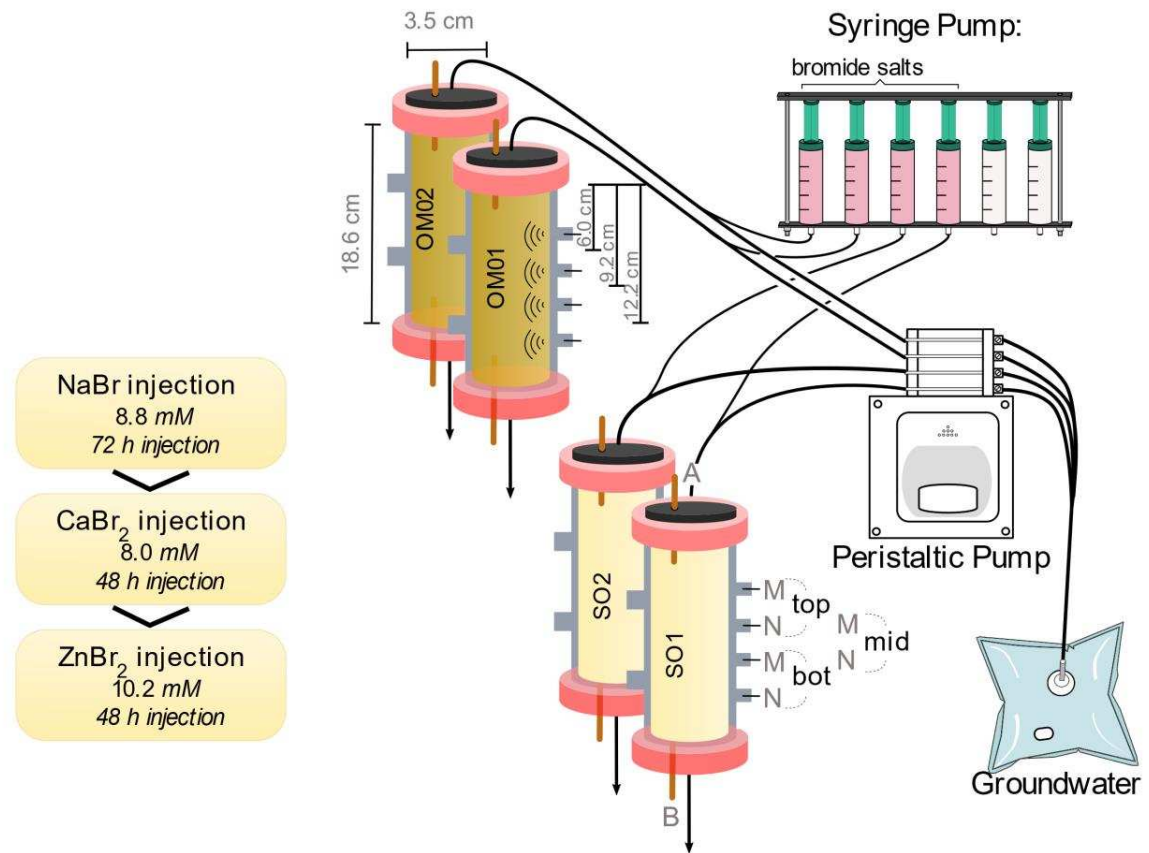
160 **2 Methods**

Figure 1: Schematic overview of the experimental set-up. Duplicate columns of sand only (S01 & S02) and sand with 20 % (w/w) solid organic matter (OM01 & OM02) were equipped with four potential electrodes (called M & N) along the flow path and two current electrodes (called A & B) at the top and bottom caps. The inflowing solution consisted of natural groundwater to which the bromide salts were added directly before the inlet using a syringe pump. Flow is from top to bottom.

2. 1 Set-Up of Flow-Through Columns

For the flow-through experiments, we packed a total of four columns and conducted the experiments at room temperature (20.5°C). Two columns were packed with a mixture of calcite (marble) sand and 20 % (w/w) solid OM (called OM01 and OM02) and the other two were packed with pure calcite (marble) sand (S01 and S02) serving as the OM-free control. The TOC content of OM01 and OM02 was 2.9%. We used the same columns, tubing, pumps and wet-

packing procedure as Strobel, Doerrich, et al., 2023. *Figure 1* shows an overview of the experimental setup and the different injection phases. Prior to packing, the marble sand was sieved to obtain a grain size distribution between 70 μm – 2 mm, washed with deionized water and submerged in a CaCl_2 bath (5 mmol L^{-1}) for 36 h to saturate charged surfaces with Ca^{2+} ions. The sand was then rinsed with CaCl_2 solution and dried at 70 °C, overnight. Targeting the application of SIP to monitor cation exchange in groundwater systems, we used a natural OM sampled from the peat layer of the Ammer floodplain aquifer, near Tübingen Germany, as the OM. The peat, described in detail in a previous study (Strobel, Doerrich, et al., 2023), was dried at 30 °C in a drying oven and homogenized after the removal of larger woody debris (>2 mm). Once packed, we sealed the columns for four weeks, for a static (no-flow) period, before starting the equilibration of the columns with pore water by pumping groundwater at a flow rate of 12 mL h^{-1} (2.2 cm h^{-1}) for 72 h (corresponding to 8.7 pore volumes) to ensure equal EC at the inlet and outlet prior to tracer injection. Groundwater from the same aquifer from which we obtained the peat, was pumped directly in the field into air-tight bags (Tedlar®, Sigma Aldrich) and stored at 10°C (mean groundwater temperature) prior to use. Before injection, the groundwater was equilibrated to reach room temperature (20°C) over 24 h. Following the equilibration, we injected 8.8 mM of NaBr during a 72 h pulse followed by a shift to pure groundwater for the subsequent 72 h. The set-up of the injection, combining a syringe pump for spiking and a main line connected to a peristaltic pump, is described in detail by Strobel, Abramov, et al., 2023. Briefly, we set a pumping rate of 0.2 mL h^{-1} at the syringe pump for spiking the inflow with NaBr, and 12 mL h^{-1} at the peristaltic pump. This guaranteed mixing of the inflow solution at the desired concentration. The subsequent injections of 8 mM CaBr_2 and 10.2 mM ZnBr_2 were injected over 48 h pulses followed by 48 h of pure groundwater, without varying the flow rates. We collected outflow samples every hour for the first 12 hours of each pulse injection, followed by 2-3 samples per day in the following days, followed by hourly samples after the shift to clean groundwater, corresponding to the desorption front. The inflow was sampled right before starting the injection and at the end of each injection.

2. 2 Sample analysis

We analyzed samples for pH and EC immediately after sample collection using handheld pH and EC electrodes (LAQUAtwin® EC-22 and pH-11, HORIBA Scientific). The samples were then

acidified (HNO₃) for cation analysis. Major anions and cations were quantified using ion chromatography (Metrohm, Germany). Zinc was measured using MP-AES (4200 MP-AES, Agilent Technologies, Australia, 213.857 nm). At the end of the experiment, we sampled the solid matrix by homogenizing the sediment of each column and measured the cation exchange capacity of the homogeneous mixture in triplicates using the ammonium-acetate method as previously described by Strobel, Doerrich, et al., 2023.

2.3 SIP measurements

Phase shift ($-\phi$) and impedance magnitude ($|Z|$) were recorded over 41 log-frequency intervals between 0.1 and 1,000 Hz using a reference resistor of 100 Ω and an amplitude of 5 V (Portable SIP Unit, Ontash & Ermac Inc., USA). The results were converted to apparent frequency-dependent complex conductivities using a geometric factor, k [m], that was experimentally determined via measurements of the apparent EC of the columns filled with water of known conductivity. SIP measurements were performed at three locations using the upper, middle, and lower potential-electrode pairs (see Figure 1). SIP measurements were performed every 30 min to 1 hour on all three potential electrode channels. For the time-series analysis, the change in complex conductivity after $t=0$ h was monitored at a frequency of 1 Hz. We chose this frequency as it exhibits no impact of high frequency noise. Choosing a different frequency would yield similar results, but with a different absolute magnitude.

2.4 Cation-Exchange and Transport Model

We simulated the cation exchange between Na⁺-Me²⁺, Ca²⁺-Mg²⁺, and Zn²⁺-Me²⁺ as competitive Langmuir sorption onto the OM. We combined the major background ions, Ca²⁺ and Mg²⁺, into one species, Me²⁺, for the model due to their similar ion exchange behavior, as done previously in Strobel, Abramov, et al., (2023). We assume that the sorption rate of cation i is proportional to the concentration of free sorption sites s_{free} (mmol g⁻¹) and to the aqueous cation concentration, c_i (mmol L⁻¹).

$$r_{sorb}^i = k_{sorb}^i \cdot c_i \cdot s_{free} \quad (1)$$

For desorption, we use a first-order rate law dependent on the sorbed cation concentration s_i (mmol g⁻¹).

$$r_{desorb}^i = k_{desorb}^i \cdot s_i \quad (2)$$

To reduce the number of parameters, we parameterized the rate constants as follows. We set $k_{\text{sorb},i} = \frac{k_{\text{desorb},i}}{K_i}$, where K_i (mmol L⁻¹) is the half-saturation constant of sorption, or the inverse of the equilibrium constant. We use the same $k_{\text{desorb},i}$ (mmol g⁻¹ s⁻¹) for Na⁺ and Ca²⁺, but allow the rate constant to differ for Zn²⁺, which forms stronger surface complexes. In the limit of $k_{\text{desorb}} \rightarrow \infty$, this formulation of kinetic sorption is mechanistically equivalent to competitive Langmuir sorption at equilibrium. Assuming that the total charge on sorption sites is limited to s_{max} (mmol g⁻¹), the concentration of free sorption sites s_{free} is given by:

$$s_{\text{free}} = s_{\text{max}} - \sum_{j=1}^N z_j \cdot s_j \quad (3)$$

where z_j is the charge of cation j , and N is the number of species. This yields the following equations for the sorbed and aqueous concentration of cation i :

$$\frac{\partial s_i}{\partial t} = r_{\text{sorb}}^i - r_{\text{desorb}}^i \quad (4)$$

$$\frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial x} - D \frac{\partial^2 c_i}{\partial x^2} = \frac{\rho_b}{n_e} (r_{\text{desorb}}^i - r_{\text{sorb}}^i) \quad (5)$$

in which, t and x denote the temporal and spatial coordinates, n_e (-) and ρ_b (g L⁻¹) are the effective porosity and bulk density, respectively, v (m s⁻¹) is the effective linear velocity. We computed the bulk density based on the solid density by $\rho_b = (1 - n_e)\rho_s$. The solid density ρ_s was estimated as 2.46 g cm⁻³ following Rühlmann et al. (2006) to account for the lower density of the OM. D (m² s⁻¹) is the dispersion coefficient, calculated from the pore diffusion coefficient D_p (m² s⁻¹) of each dissolved ion and the dispersivity α (m) of the OM-sand mix, using the approach of Scheidegger (1961): $D = D_p + \alpha v$. For the Zn²⁺ injection experiment, we consider the precipitation of zinc carbonate (Patterson et al., 1977) as a first-order reaction:

$$r_{\text{precip}} = -k_{\text{precip}} \cdot c_{\text{Zn}^{2+}} \quad (6)$$

with the rate constant k_{precip} [s⁻¹]. Equation (6) was added to the term in brackets on the right-hand side of equation (5) for the Zn²⁺ case.

The initial conditions were based on the assumption that aqueous and sorbed concentrations are at equilibrium. Using the known composition of the injected groundwater for solute concentrations, we computed the initial sorbed concentrations $s_{0,i}$ as follows:

$$s_{0,i} = s_{\max} \frac{c_i}{K_i \left(1 + \sum_{j=1}^N z_j \frac{c_j}{K_j} \right)} \quad (7)$$

At the inflow boundary, we fixed the concentrations to the values in the inflow solution. At the outflow boundary, we assumed the dispersive flux to be zero and considered only the advective transport out of the column.

We discretized Equations 4 and 5, which describe transport and reactions in the column, using a finite volume approach. The system of ordinary differential equations obtained from discretization was solved using a Backwards Differentiation Formula (Byrne & Hindmarsh, 1975; Jackson & Sacks-Davis, 1980) using the Python library Sunode (Seyboldt et al., 2024) which wraps the CVODES module of the SUNDIALS library (Hindmarsh et al., 2005; Serban & Hindmarsh, 2008).

2.4.1 Implementing $\Delta\sigma''$ as a Proxy for the Sorbing-Phase Concentrations

For the parameter estimation we combined knowledge of the aqueous phase concentrations at the outflow with knowledge of the change in sorbed concentrations as inferred from $\Delta\sigma''$, the change in imaginary conductivity. To directly compare the simulated sorbed concentrations to $\Delta\sigma''$, we assume that $\Delta\sigma''$ can be decomposed into contributions of the ion exchange in the electrical double layer (EDL), $\Delta\sigma''_{IE}$ ($\mu\text{S cm}^{-1}$), and the ionic strength of the bulk fluid to the change in polarization, $\Delta\sigma''_{EC}$ ($\mu\text{S cm}^{-1}$):

$$\Delta\sigma'' = \Delta\sigma''_{IE} + \Delta\sigma''_{EC} = \Delta\sigma''_{IE} + a \cdot c_{Br^-} \quad (8)$$

In which a ($\mu\text{S L cm}^{-1} \text{ mmol}^{-1}$) is the linear proportionality constant between the aqueous concentration of bromide c_{Br^-} (mmol L^{-1}) at the midpoint of the potential electrode pair and $\Delta\sigma''_{EC}$. This approach is based on the assumptions that (1) c_{Br^-} is a proxy for the change in EC and (2) that the relationship is linear. Weller et al. (2011) found a power law relationship with an exponent of around 0.5 between salinity and the imaginary conductivity in sandstone samples. In our experiments the EC ranged from 800 to 2600 $\mu\text{S cm}^{-1}$, a much narrower range than the 250 to $23 \cdot 10^3 \mu\text{S cm}^{-1}$ used by Weller et al. (2011) so we decided to assume the simplest possible, linear relationship. In experimental phases where we did not expect major changes in the chemical composition of the EDL while the EC was changing, we observed a satisfactory linear relationship between c_{Br^-} and $\Delta\sigma''$ (see figure S1 in the supporting information) making us confident that this is a good first approximation of this clearly more complex relationship.

Secondly, we estimated a compound-specific proportionality constant p_{inj} ($\mu\text{S g cm}^{-1} \text{ mmol}^{-1}$) between the sorbed concentration of the injected cation and $\Delta\sigma''_{IE}$ that enabled a direct link between $\Delta\sigma''_{IE}$ and the resulting sorbed concentration s_{inj} ($\text{mmol g}^{-1}_{\text{sed}}$) at the midpoint of the electrode pair:

$$\Delta\sigma''_{IE} = p_{inj} \cdot s_{inj} \quad (9)$$

2.4.2. Parameter Inference by the Markov Chain Monte Carlo Method

We estimated parameters using a Bayesian approach, which yields parameter distributions rather than single values to account for uncertainty. This approach requires defining prior distributions of the parameter values that represent expert knowledge about reasonable parameter ranges. These distributions are then updated with a likelihood function which can be interpreted as a goodness-of-fit measure of the model to the data. The resulting posterior distribution represents the remaining uncertainty in the parameters after the model has been fitted to the data.

Parameters that were set to fixed values in the simulation are shown in Table S1 in the supporting information. We defined prior distributions based on physical constraints, literature values, and order-of-magnitude estimates (see Table S2 in the supporting information). For the likelihood, we used concentration time series of injected and background ions (c_{inj} and c_{bg}) at the column outflow, and $\Delta\sigma''$ at the three SIP measurement locations. We assumed that the data are normally distributed around the simulated values, with a fixed standard deviation per data type.

We sampled the posterior distribution with a Sequential Monte Carlo (SMC) algorithm using the Python package PyMC (Abril-Pla et al., 2023). We generated 2000 posterior samples in 4 independent chains (i.e., 500 samples per chain). To assess convergence, we computed the $\hat{R}$ -criterion (Vehtari et al., 2021) using the ArViz library (Kumar et al., 2019).

3 Results and discussion

Figure 2 shows σ'' spectra measured at 6 cm from the inlet at selected time points for all three cation-injection experiments (Na^+ , Ca^{2+} and Zn^{2+}) in the OM-containing treatment. (Note: all spectra are shown in Figure S2-3 in the supporting information). The spectra show a gradual increase from low to higher frequency reaching a peak above 10 Hz. Since the spectral characteristics were similar across all experiments we conclude that a similar type of polarization

(and thus reaction) process took place in all experiments. The lack of frequency-dependent changes of σ'' suggests that this process affects a wide range of polarization length scales, as can be expected from cation exchange on a heterogeneous matrix as organic matter. In the pure-sand control columns, σ'' was close to the detection limit and did not change over time in all experiments (see Figure S4-5 in the supporting information), indicating the absence of appreciable cation exchange. This was fully confirmed by the outflow concentration data for the NaBr and CaBr₂ injection (see Figure S8-9 in the supporting information). For the ZnBr₂ injection we observe some evidence for cation exchange also in the pure sand columns which is however much faster and lower in magnitude compared to the OM containing columns (data are shown and discussed in section 3.2 in detail). Therefore, we focus in the following on a time-series analysis of the OM-containing column, and present σ'' values at the single frequency of 1Hz (highlighted by red crosses in *Figure 2*). We chose that frequency to avoid any effects of measurement noise at high-frequency. Both OM-containing columns showed a generally similar behavior. However, the dataset in OM02 was interrupted by unwanted peaks of high salt concentration, caused by errors when changing the syringe pump. Thus, we focus our time-series analysis on OM01 but present all data of OM02 in the supporting information (Figures S6 and S10).

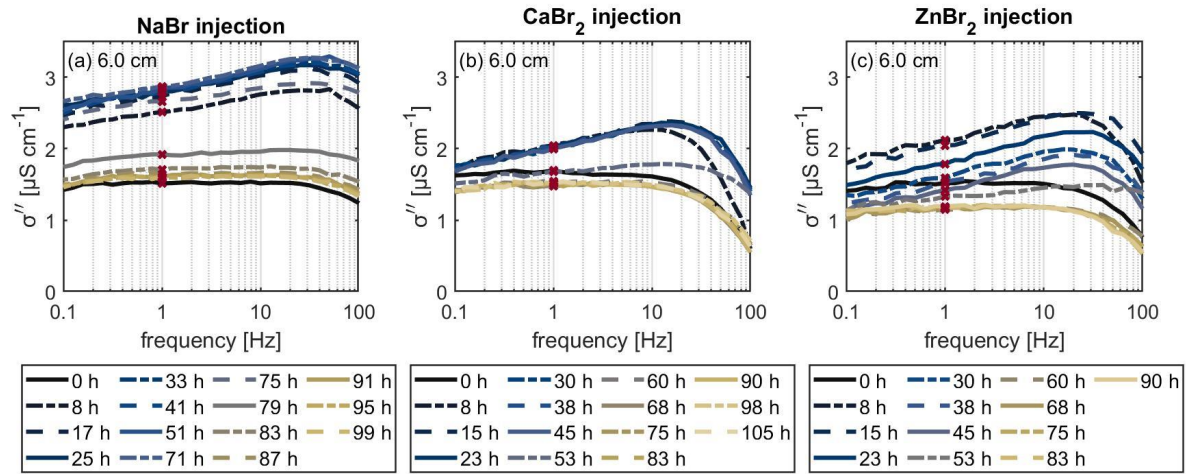


Figure 2: Selected imaginary conductivity (σ'') spectra during the (a) Na^+ -, (b) Ca^{2+} - and (c) Zn^{2+} -injection experiments at the SIP measurement location closest to the inlet (6 cm) in column OM01. (Note: Na^+ was injected for 72 h whereas Ca^{2+} and Zn^{2+} for 48 h). The red crosses mark the measurements at 1 Hz, presented henceforth for time-series analysis. The spectra are truncated at 100 Hz due to noise at higher frequencies.

3.1 Qualitative interpretation of SIP data

In Figure 3 we compare the change in real and imaginary conductivity as gray, dashed lines and colored lines, respectively, in column OM01. The corresponding phase shifts and impedances are shown in Figure S7 in the supporting information. Columns of subplots represent experiments with different cation injections, rows of subplots represent different locations of SIP measurements, i.e. with increasing distance from the inlet. For a direct comparison across potential electrode pairs (6, 9.2 and 12.2 cm) and experiments, the axes limits are held constant in all panels and signals are plotted as the difference, Δ , between measurement and the baseline prior to cation injection. The arrival time, and pulse duration of the conservative anion, Br^- , is captured by $\Delta\sigma'$ (Ben Moshe et al., 2021; Strobel, Abramov, et al., 2023) in all cases. The increase in $\Delta\sigma'$ was the lowest during the NaBr injection, owing to the Na-Br mole ratio, yielding only half of the bromide concentration injected during the CaBr₂ and ZnBr₂ injections (injected cation concentration in all cases: 8 - 10 mmol L⁻¹).

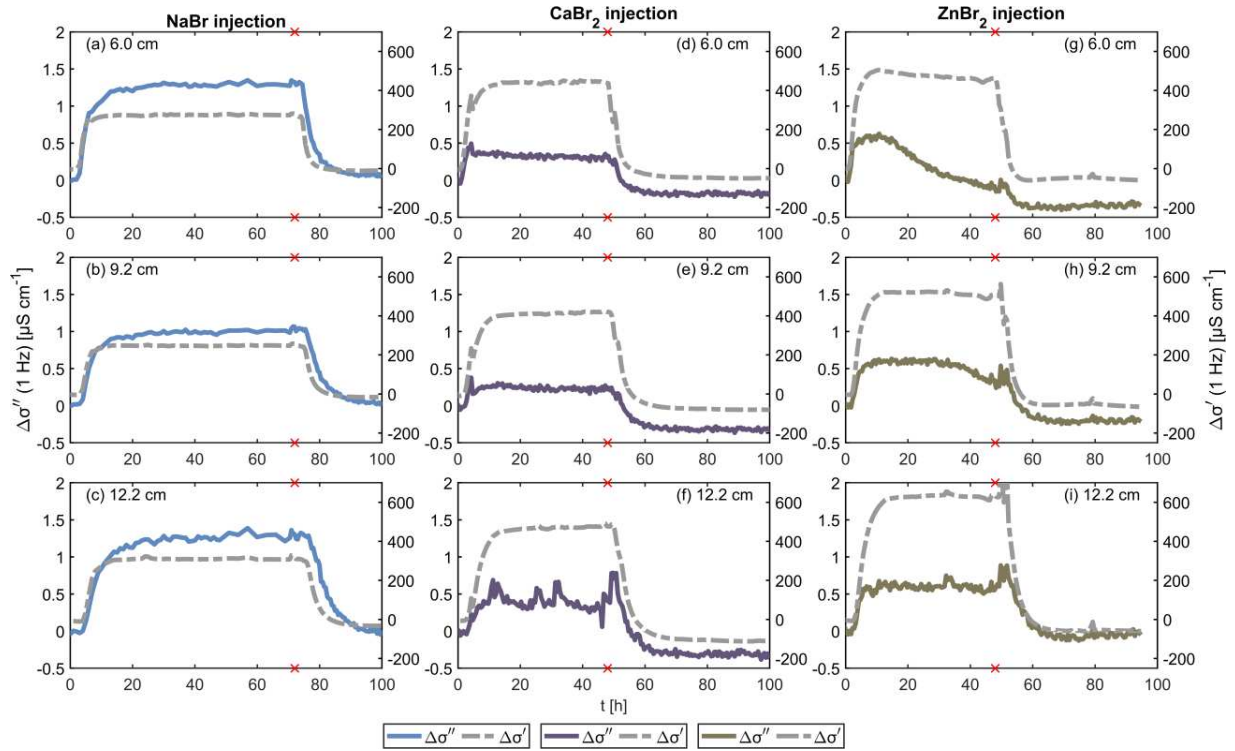


Figure 3: Comparison of the change (Δ) in real ($\Delta\sigma'$) and imaginary conductivity ($\Delta\sigma''$), at 1 Hz, during all three cation injections: NaBr (a – c), CaBr_2 (d – f) and ZnBr_2 (g – i). Red crosses on the x-axis mark the end of each injection, where NaBr, CaBr_2 , ZnBr_2 were injected for 72, 48 and 48h, respectively. Subplot rows depict all three SIP-measurement locations shown here for column OM01, where the distance corresponds to the midpoint of the potential electrode pair relative to the inlet.

The major background cations in the pore water were Ca^{2+} and Mg^{2+} , at 3.45 and 1.75 mmol L⁻¹, respectively. Owing to their similar hydrated radii (412 and 428 pm (Amelung et al., 2018)), valence and complexation capabilities, that in turn yield similar ion mobilities (Revil et al., 1998) in the EDL, we did not expect a strong effect of Ca^{2+} - Mg^{2+} exchange on σ'' . The CaBr_2 injection (Figure 3 d – f), therefore, served as the injection pulse during which EC effects dominate over changes in the EDL composition. In agreement with our expectation, the $\Delta\sigma''$ for the CaBr_2 injection is the lowest of all three cation-injection experiments and across all locations of SIP measurements.

During the NaBr injection (Figure 3 a – c), $\Delta\sigma''$ increased up to 1 – 1.4 $\mu\text{S cm}^{-1}$ (depending on the SIP location) and stayed constant at its maximum value until the NaBr was stopped after 72 h

and σ'' dropped again to the initial value (i.e. $\Delta\sigma'' = 0$). The increase in polarization is driven by the higher concentration of more mobile Na^+ ions in the EDL, relative to the lower mobility background divalent cations. The separate conduction and polarization controls on σ' and σ'' , respectively, become particularly evident at 12.2 cm where a time-lag can be observed between the increase and decrease of $\Delta\sigma'$ and $\Delta\sigma''$. The time delay points to the retention (i.e., sorption or ion-exchange) of Na^+ in the matrix relative to the conservative transport of Br^- at the flow velocity. Moreover, the maximum $\Delta\sigma''$ is about four times higher than during the CaBr_2 injection. Both the retarded $\Delta\sigma''$ -front and the maximum $\Delta\sigma''$ support our hypothesis that a significant fraction of Na^+ exchanged Ca^{2+} and Mg^{2+} in the OM-sand matrix, similar to previously reported findings by (Strobel, Abramov, et al., 2023).

The ZnBr_2 injection (*Figure 3 g – i*), yielded a spatially variant trend in the SIP measurements. At all locations, there was an increase in $\Delta\sigma'$ and $\Delta\sigma''$ as a result of the ZnBr_2 injection and a decrease in $\Delta\sigma'$ and $\Delta\sigma''$ once the injection was stopped. However, unlike the plateau that developed during the Na^+ and Ca^{2+} injections, the ZnBr_2 led to a drop in $\Delta\sigma''$ at 6 cm (*Figure 3 g*) following the initial increase (at 10 h), from $+0.6 \mu\text{S cm}^{-1}$ to $-0.15 \mu\text{S cm}^{-1}$, despite the fact that Zn^{2+} was continuously injected for 48 hours. Similarly (but delayed), at 9.2 cm from the inlet (*Figure 3 h*), $\Delta\sigma''$ stayed constant at $+0.6 \mu\text{S cm}^{-1}$ until 34 h, followed by a decrease to $0.25 \mu\text{S cm}^{-1}$ at 48 h, whereas no decrease at all was observed at 12.2 cm. The different temporal trends are directly evident when comparing the ZnBr_2 with the CaBr_2 case and agree with our hypothesis that exchange of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions by the more strongly complexing Zn^{2+} ions results in a decrease of σ'' . The fact that we observe the strongest decrease of $\Delta\sigma''$ closest to the inlet and no decrease at 12.2 cm suggests that Zn^{2+} ions were completely sorbed in the upper half of the column, agreeing well with the fact that we did not detect any Zn^{2+} breakthrough at the outlet (see details below). After the stop of the injection, $\Delta\sigma''$ stabilized at $-0.1 \mu\text{S cm}^{-1}$ (12.2 cm) to $-0.35 \mu\text{S cm}^{-1}$ (6 cm), highlighting that the pre-injection equilibrium was not reached within the time of the experiment and that the difference in EDL composition is highest close to the inlet where the Zn^{2+} was sorbed. This suggests that the desorption of Zn^{2+} was considerably slower than its adsorption.

3.2 Coupling concentration and $\Delta\sigma''$ -data

The concentration measurements at the column outlet confirm the qualitative interpretation of $\Delta\sigma''$ discussed in the previous section. In *Figure 4*, the concentrations of the injected cations, the background cations, and of the conservatively behaving anion, Br^- , are shown for all three injection experiments. When presenting the NaBr - and ZnBr_2 -injection, we combine the concentrations of Ca^{2+} and Mg^{2+} into a single species, Me^{2+} , as they show a very similar behavior (*Figure 4 d&f*). Only in the case of the Ca^{2+} -injection we distinguish the two species, because in this case their slightly different sorption behavior becomes relevant (*Figure 4 b&e*). Cation exchange is evident in all three injection experiments via the measured increase in the concentration of the background ion (Me^{2+} for Na^+ and Zn^{2+} and Mg^{2+} for Ca^{2+}) during breakthrough of the injection front (*Figure 4 d-f*). In the NaBr -injection experiment, ion exchange reaches equilibrium across the entire columns with Na^+ - and Me^{2+} -concentrations both reaching the inflow concentration at the outlet (*Figure 4 a&d*). Conversely, for CaBr_2 and ZnBr_2 this is not the case. As already postulated based on the $\Delta\sigma''$ data, the sorption of Zn^{2+} onto OM is stronger than that of Me^{2+} , and thus prevents its breakthrough at the outlet (*Figure 4 c*), yielding a strong release of background Me^{2+} -ions (*Figure 4 f*). For CaBr_2 , the very similar sorption strengths of Ca^{2+} and Mg^{2+} result in a quick local reequilibration that is only changing gradually.

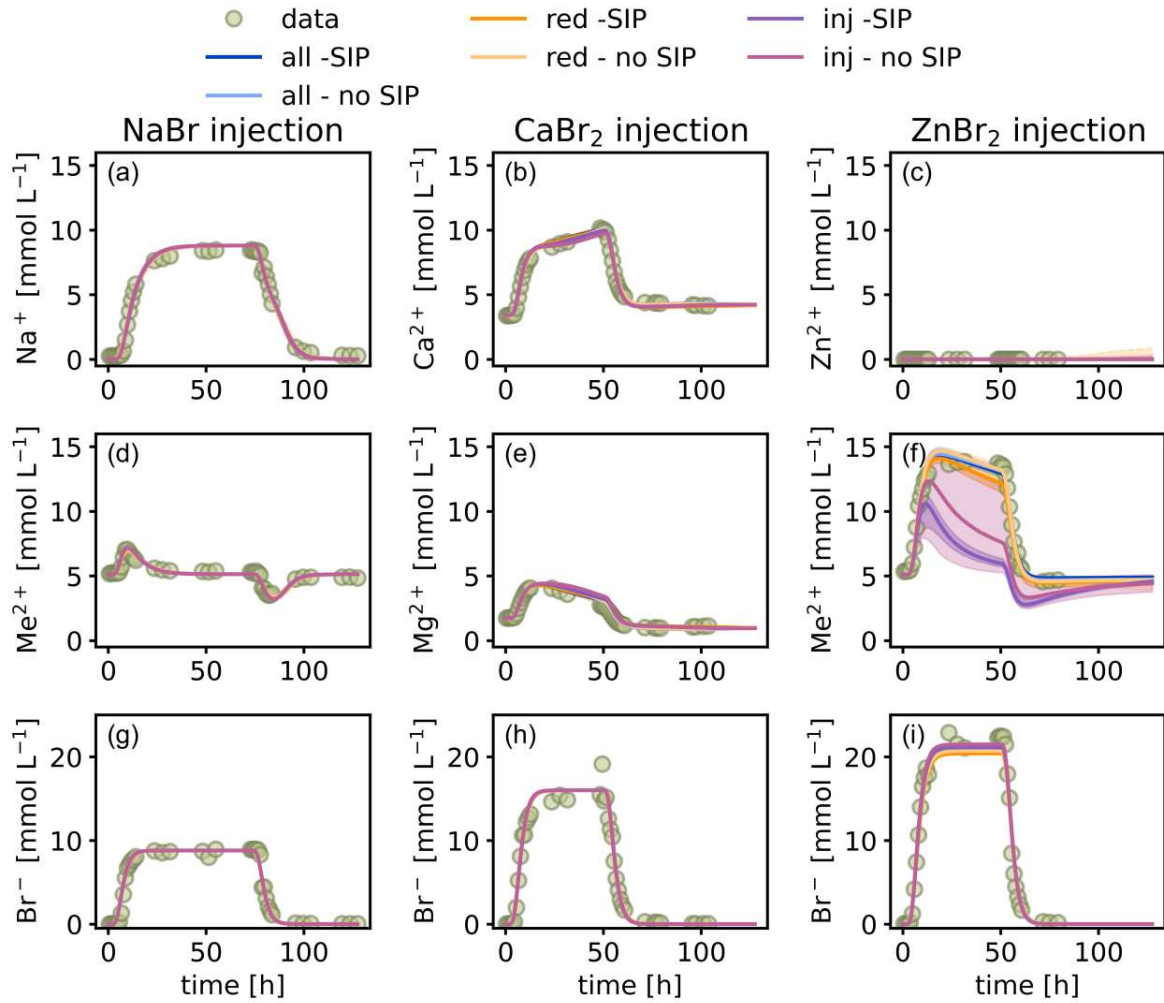


Figure 4: Simulated concentrations at the column outlet of injected cations (a-c), the corresponding background or competing cations (d-f) and the conservative anion Br^- (g-i) for the three different injections. During the NaBr and ZnBr_2 injections Mg^{2+} and Ca^{2+} concentrations are lumped as Me^{2+} , whereas in the CaBr injection, Mg^{2+} is the sole competing ion and is shown individually. Six modeling scenarios are compared that rely on varying amounts of data for parameter estimation: all concentration data with or without SIP (all-SIP or -no SIP), every 3rd concentration data point with or without SIP (red-SIP or -no SIP), only the injected cation concentrations with or without SIP (inj-SIP or -no SIP). The different parameter estimation scenarios fall on top of each other in the Na^+ and Ca^{2+} experiments, and differences are only discernible in panels (f) and (i). The shaded areas show the range between the 5th and 95th quantile of the fit.

We simulated the transport and ion exchange reaction to confirm our interpretation of the reactive processes. By incorporating the $\Delta\sigma''$ data into the parameter estimation scheme, as a proxy for the sorbed concentration of the injected cation, we investigate the potential additional information that can be gained from measuring SIP alongside geochemical sampling schemes. We estimated the parameters six times based on a combination of three different datasets of concentration data either with or without the SIP data as additional information: Using all available data (*all – SIP and all – no SIP*), using every 3rd concentration data point and the SIP data (*red – SIP and red – no SIP*) or using only the concentration time series of the injected cation (*inj – SIP and inj – no SIP*). The resulting fits of the six scenarios are shown alongside with the data in *Figure 4*. The results show that our model can accurately predict both conservative transport (*Figure 4 g-i*) and the cation-exchange processes in the NaBr- and CaBr₂-injection experiments (*Figure 4 a-b&d-e*) with only minor variations between the different scenarios. In these cases, the concentration time series of the injected cation in the outlet or using only a subset of the data were sufficient to constrain the model, and the addition of SIP measurements did not improve the calibration outcome. It is noteworthy, that the inclusion of the SIP data slightly reduces the parameter uncertainty of the sorption parameters $K_{Zn, \text{ sorb}}$ and $K_{Me, \text{ sorb}}$ (see *Figure 6* and *Figures S12-14* in the supporting information).

However, in the ZnBr₂-injection experiment, we observe a major difference between the calibration scenarios, with and without the concentration data of the background cation. Because Zn²⁺ did not break through during the experiment, the Zn²⁺ time-series does not provide sufficient information to constrain the model and accurately predict the Me²⁺-concentrations (*Figure 4 f*, pink line), which is also highlighted in the high uncertainty of the model fit when using only the Zn²⁺ data (shown by the shaded pink area). Adding information about the sorbing-phase concentrations by incorporating the SIP data reduces the model uncertainty, but does not improve the fit (*Figure 4 f*, purple line & area). We speculate that either the formulation of our ion-exchange model or the linear proportionality between the sorbing-phase concentration and $\Delta\sigma''$ do not fully capture the processes relevant for the complexation of Zn²⁺. Zn²⁺ is a heavy-metal ion that interacts differently with charged surfaces than the ions of the alkaline (earth) metals Na⁺, Ca²⁺, and Mg²⁺ (Amelung et al., 2018; Himes & Barber, 1957; Randhawa & Broadbent, 1965). It is therefore reasonable to expect that the reaction mechanism is not fully described by our 2nd-order formulation. This could also explain the difference of the simulated

Me²⁺ concentrations (*Figure 4 f*) when using all available data compared to the measurements. They exhibit an almost constant plateau, rather than showing a gradual decrease of the Me²⁺ concentrations as predicted by the model. In addition, we had to add a first-order precipitation term to the model to account for zinc-carbonate precipitation in the bicarbonate dominated groundwater in order to prevent the model from predicting a breakthrough of Zn²⁺. This additional degree of freedom might not be constrained by our data even when adding the SIP data. In the absence of background concentration data (*inj-SIP* case), the model predicts an order of magnitude higher precipitation rates and consequently a much lower fraction of sorbed Zn²⁺ (see *Figure S11*) compared to the other scenarios. Finally, while in theory, the zinc carbonate precipitation could have also caused calcite dissolution, the excellent agreement of our model with the Zn²⁺ and Ca²⁺/Me²⁺ concentration provides strong evidence to suggest that there was no additional source of Ca²⁺ ions. Moreover, the fact that we do not observe unexpectedly high Ca²⁺ concentrations in the control (marble sand only) columns (see *Figures S8 and S9* in the supporting information) further suggests that we included all relevant processes into our reactive transport model, and justify the omission of calcite dissolution.

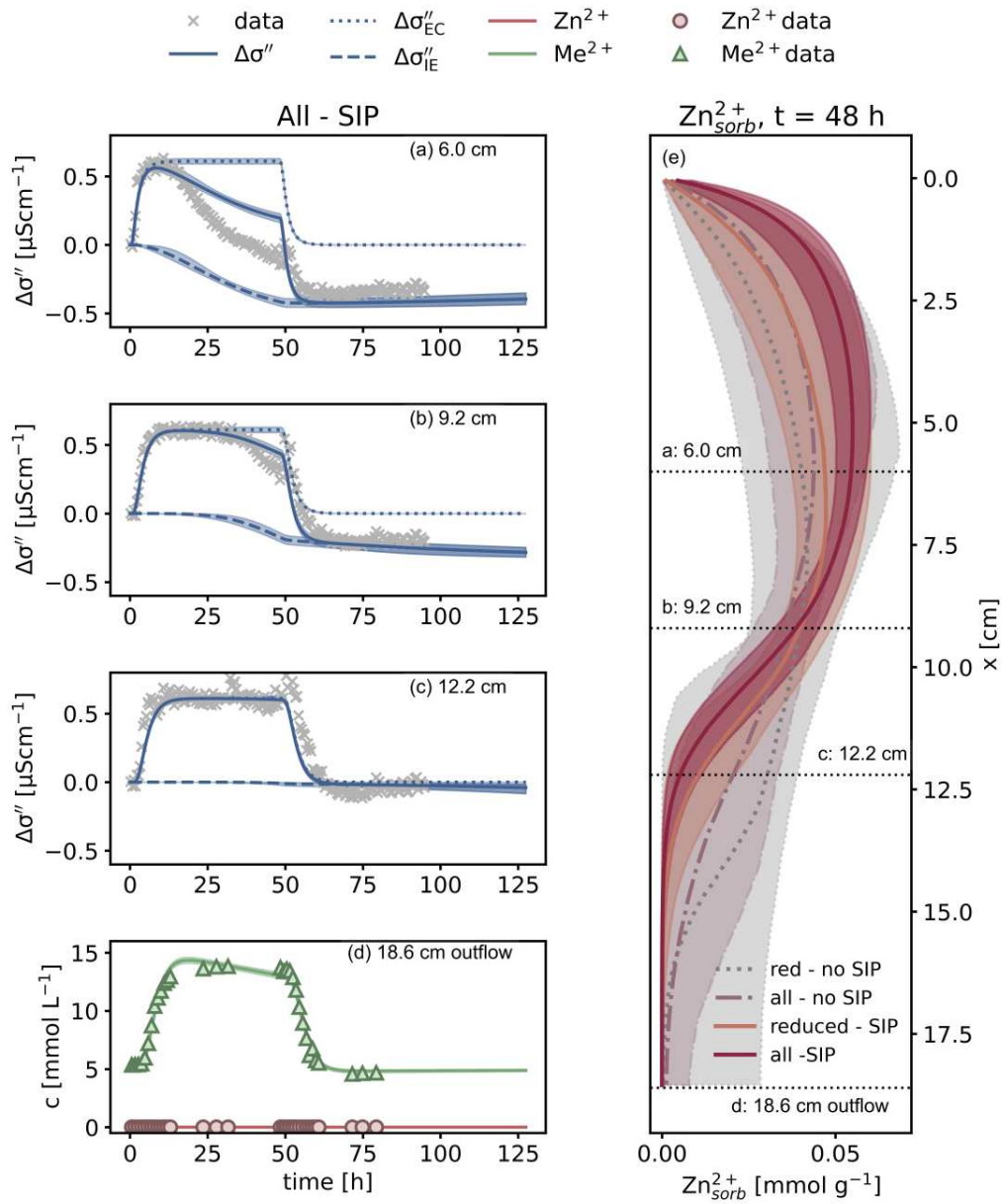


Figure 5. Model-data comparison of the simulation of the Zn^{2+} -experiment using all geochemical data, all-SIP (left panels). Panels (a–c) show the the simulated change (Δ) in imaginary conductivity ($\Delta\sigma''$) compared to measured $\Delta\sigma''$ at all SIP measurement locations. In addition, the contribution of electrical conductivity, $\Delta\sigma''_{\text{EC}}$, and ion exchange, $\Delta\sigma''_{\text{IE}}$, to the overall change in σ'' are shown separately as dotted and dashed lines, respectively. Panel (d) compares simulated versus measured concentrations. Simulated sorbed concentration profiles of Zn^{2+} at the end of the experiment are shown for selected parameter estimation scenarios (e). The dashed

lines in the panel denote the location of the SIP measurements and the outflow and the shaded areas show the range between the 5th and 95th quantile.

In Figure 5 we show the model-data comparison for the outflow concentration measurements (d) alongside with the fit of the SIP data (a-c) for the scenario with all data used for parameter estimation. In addition, Figure 5e shows the simulated Zn^{2+} concentrations at the end of the ZnBr₂-injection for the all chemistry and reduced chemistry data case. The fit to the SIP data for the other scenarios and the corresponding profiles are shown in the supporting information figure S10-11, but differences in the fit to the SIP data between the scenarios are subtle. In the following, we compare the different parameter-estimation scenarios in more detail and focus our analysis on the ZnBr₂ injection, because of the spatial variability in the extent of the Zn^{2+} sorption inferred from our qualitative interpretation of the SIP data. The corresponding figures for the other two injection experiments are presented in the supporting information Figure S8-9. In all parameter-estimation scenarios the contribution of the EC to $\Delta\sigma''$ is similar and explains the initial increase of $\Delta\sigma''$ at all measurement locations. The model predicts a negative proportionality between sorbed Zn^{2+} concentration and $\Delta\sigma''$ that agrees with our hypothesis that the lower ion mobility of Zn^{2+} compared to $\text{Ca}^{2+}/\text{Mg}^{2+}$ results in a decrease in σ'' . The general temporal trends of the model agree with trends in the SIP data for both cases but underpredict the decrease of $\Delta\sigma''$ driven by Zn^{2+} sorption, in particular at 6.0 cm (Figure 5 a). A difference between the scenarios with and without SIP data lies in the position of the Zn^{2+} sorption front (Figure 5e) for both, the all chemistry and reduced chemistry scenario. With the information at the SIP electrodes, the uncertainty is considerably reduced and sorption is constrained to occur primarily before the 2nd electrode pair at 9.2 cm.

While all models yield similar model parameters (Figure 6), incorporating SIP data in the calibration scheme yields slightly lower parameter uncertainties. This highlights a potentially important additional information gained from its inclusion. Kernel density estimates of the posterior distributions of parameters not shown in Figure 6 are shown in Figures S15-S17 of the supporting information alongside with the mean parameter estimates of the ‘all-SIP’ scenario in table S3.

The linear $\Delta\sigma''$ - $\text{Zn}_{\text{sorb}}^{2+}$ relationship we chose is probably an oversimplification of reality. Yet, it is striking how well this approach can reflect the general reaction trends. In our formulation, we neglect any effect of the zinc precipitate on the signal due to its low volume fraction and the

504 generally high abundance of carbonates in the background solid matrix. In the upper section of
505 the column (6.0 and 9.2 cm), where Zn^{2+} -sorption is taking place, however, the measured
506 decrease in $\Delta\sigma''$ at the end of the ZnBr_2 injection (at around 50 h), driven by the decrease in EC,
507 is not as pronounced as that predicted by the model nor measured during the corresponding
508 increase at the onset of injection (0 to 10 h). As this is only the case for the ZnBr_2 injection and
509 does not happen in the other two experiments, we speculate that we still miss a process either in
510 our conceptual model of induced polarization or the behavior of Zn^{2+} in this system.

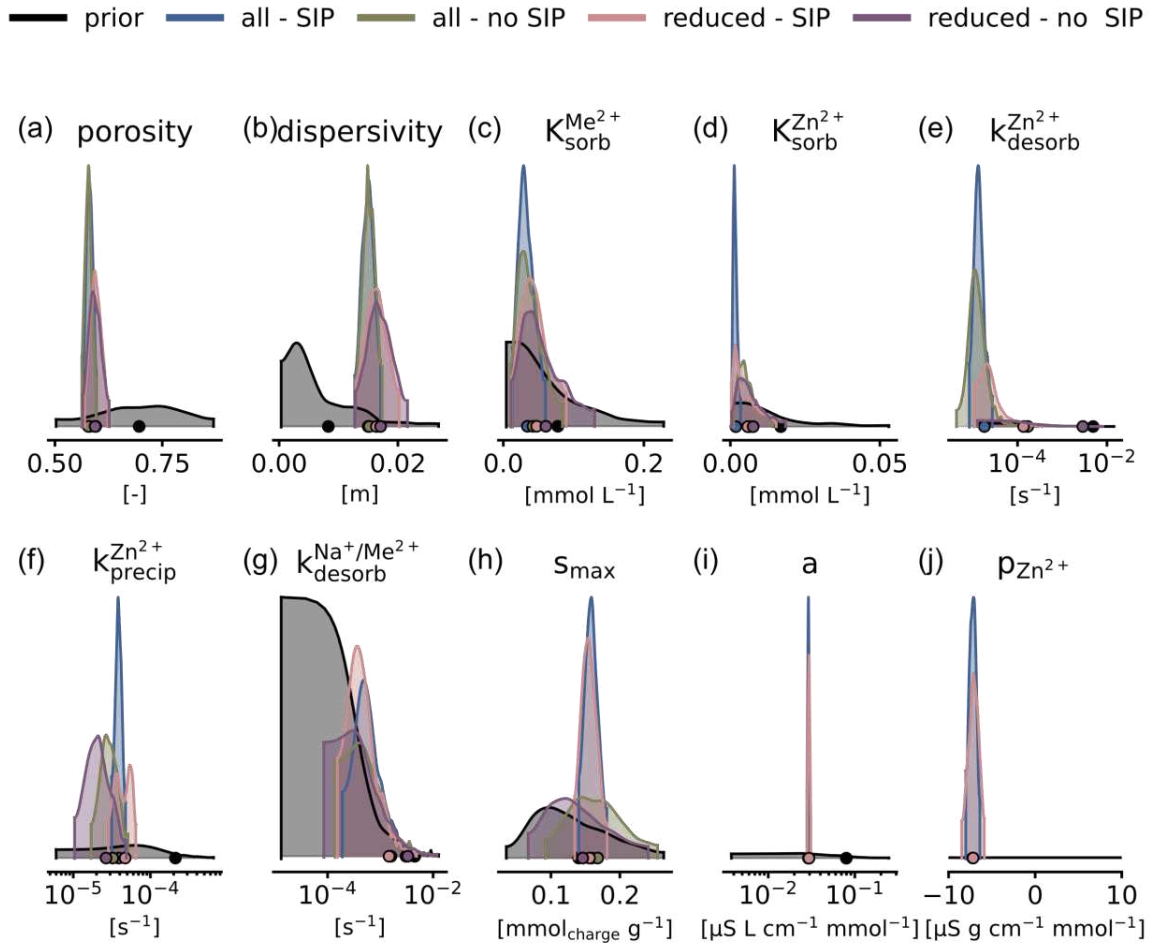


Figure 6: Kernel density estimates of the prior and posterior distributions of parameters relevant for the Zn^{2+} experiment. The posterior distributions are shown for the different scenarios of all concentration data or a reduced dataset of every 3rd datapoint with or without SIP data. Plots are cut at the 94 % highest density interval.

4 Opportunities and Limitations for Reaction Monitoring with SIP

The present experiment exemplifies that SIP facilitates monitoring of reactions in the subsurface, but also highlights its limitations. The qualitative interpretation of complex-conductivity data is hampered by changes of electrical conductivity (EC) modifying $\Delta\sigma''$. Thus, it can be advantageous to maintain constant EC or at least have phases of stable EC during the reaction phase (Ben Moshe & Furman, 2022; Mellage, Zakai, et al., 2022). The approach outlined in this study accounts for EC changes, potentially extending the applicability of SIP to more dynamic

systems. For instance, data from a (groundwater) tracer test could be utilized to calibrate the relationship between EC and $\Delta\sigma''$, which could then be applied to the main / target experiment. However, care must also be taken in the design of the tracer test, as the injection of a salt at high concentration will inevitably result in ion exchange. The qualitative interpretation of SIP data in dynamic systems requires a solid understanding of the relevant processes. Its complexity arises from the multitude of parameters that can affect the SIP signal and calls for the comprehensive monitoring of background chemistry (i.e. EC, pH, redox potential and concentration of major ions) during an experiment. The interpretation is further complicated by the absence of direct, quantitative links between geophysical measurements and geochemical parameters in such complex systems. Consequently, sufficient prior knowledge and experience is essential for effectively utilizing SIP in reaction monitoring.

The incorporation of SIP data into reactive-transport modeling schemes has been proposed (Kessouri et al., 2019), however the lack of petro-physical relationships that link specific processes to their σ'' signal is hampering its application. With the simple relationships in this work we demonstrate how quantitative coupling may be implemented. Yet, we acknowledge that the additional information gained, in most of our cases, was limited, and that the SIP data cannot fully replace concentration data of a reactive species. However, this is dependent on the target reactive process to be monitored and the availability of highly resolved concentration data. It is worth noting, that the incorporation of SIP data improved parameter estimation. Despite these limitations, the framework presented here demonstrates the potential for such integrated approaches and their applicability to various reactive scenarios. This coupling could lead to more accurate and comprehensive models, help identifying missing processes and thereby advance our capability to monitor and interpret complex geochemical processes in situ.

5 Conclusions

The absence of changes in $\Delta\sigma''$ in the control columns without OM showed that electrochemical polarization is restricted to the organic matter in our system. The experiment was therefore suitable to examine whether the existing electrochemical polarization theory for mineral surfaces is also applicable to OM. The excellent agreement between our hypotheses on the effect of

different cations on σ'' and the resulting $\Delta\sigma''$ (Figure 3) suggests that OM polarization qualitatively follows similar principles as electrochemical polarization on mineral surfaces.

We were successful at monitoring conservative transport and cation exchange on OM through the interpretation of $\Delta\sigma''/\Delta\sigma'$ -plots only. These plots condense information stemming from the multidimensional SIP measurements into a format that can be quickly evaluated and is thus valuable in the monitoring of column or other time-lapse experiments.

To do so, it is important to estimate the expected effect of a certain reaction on σ'' . In this study, we focus on changes in the surface ion mobility of different cations in the EDL. This implies that during the reaction the surface charge density does not change dramatically. Quantitative estimates of the surface ion mobility are often not available. Therefore, polarization models assume a fraction of the mobility in water (Revil et al., 1998; Vaudelet et al., 2011). This yields very similar ion mobilities and thus similar σ'' measurements should be expected for Ca^{2+} and Zn^{2+} , contradictory to our experimental results. The ion mobility in water is controlled primarily by the valence of the ion and its size and neglects any non-electrostatic interactions (e.g. surface-complexes) that can exist between the surface and the ion. Based on our experimental results and the resulting conceptual model we find it promising, from a geochemist's experimental perspective, to rely more on sorption coefficients to estimate ion mobilities for polarization models rather than relying on their diffusion coefficients in water. Sorption coefficients integrate all ion-surface interactions and can often be found in literature for different materials. In our experiment the estimated half-saturation concentrations or Langmuir-type sorption constants of the three cations differ by one order of magnitude (Figure 7), which agrees with the observed effects on σ'' .

The experiment presented here is a proof-of-concept on how (S)IP data can be incorporated in reaction monitoring of reactions involving charged surfaces. The results of our reactive-transport model show how SIP data can quantitatively be coupled with geochemical data sets. Separating the changes in $\Delta\sigma''$ caused by changes in electrical conductivity from those caused by the reaction can (1) enhance the interpretability of SIP signals in dynamic systems, (2) help to identify overlooked processes, and (3) facilitate assessing the relative effect of different processes on σ'' , in particular, through iterative steps between conceptual and mathematical modeling.

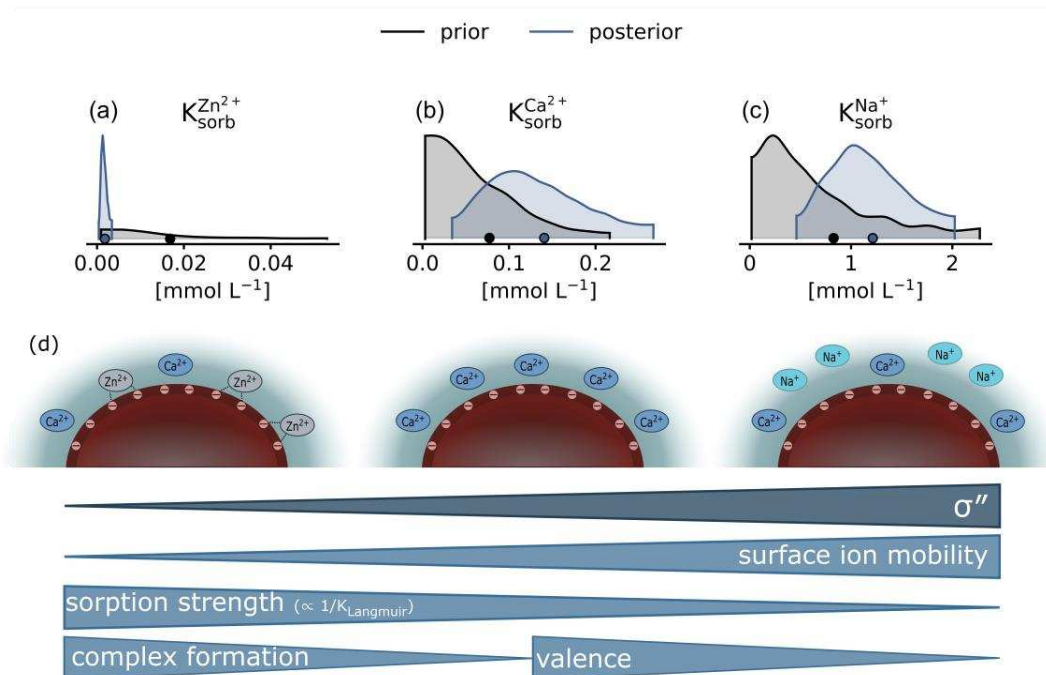


Figure 7. Prior and posterior kernel density distribution of the sorption half-saturation constants of the injected cations (a-c) of the scenario where all available data were used for parameter estimation. A schematic representation of the relationship between sorption of cations on organic matter and their respective effect on σ'' is shown in (d).

Acknowledgments

Adrian Mellige would like to acknowledge the financial support of the Baden-Württemberg Stiftung received for this project via the Eliteprogramme for Postdocs as well as the financial support of the Ministry for Science, Research and the Arts of Baden-Württemberg via the Research Seed Capital Program (RiSC). We thank Björn Spranglewski for his support with the IC measurements and Manuel Dörrich and Emma-Helen Stieff for help conducting the experiment. Open Access funding enabled and organized by Projekt DEAL. We are grateful to Matthias Bücker, two anonymous reviewers, and the Associate Editor, Lee Slater, whose constructive remarks have helped improve the paper.

Open Research

The SIP data, the geochemical data and the Python codes for the reactive transport modeling are available at <https://doi.org/10.5281/zenodo.12788754> under the MIT license (Strobel, 2024).

References

Abril-Pla, O., Andreani, V., Carroll, C., Dong, L., Fonnesbeck, C. J., Kochurov, M., Kumar, R., Lao, J., Luhmann, C. C., Martin, O. A., Osthege, M., Vieira, R., Wiecki, T., & Zinkov, R. (2023). PyMC: A modern, and comprehensive probabilistic programming framework in Python. *PeerJ Computer Science*, 9, e1516. <https://doi.org/10.7717/peerj-cs.1516>

Albers, C. N., Banta, G. T., Hansen, P. E., & Jacobsen, O. S. (2009). The influence of organic matter on sorption and fate of glyphosate in soil – Comparing different soils and humic substances. *Environmental Pollution*, 157(10), 2865–2870. <https://doi.org/10.1016/j.envpol.2009.04.004>

Amelung, W., Blume, H.-P., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K., & Wilke, B.-M. (2018). *Scheffer/Schachtschabel Lehrbuch der Bodenkunde* (F. Scheffer & P. Schachtschabel, Trans.; 17., überarbeitete und ergänzte Auflage). Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-662-55871-3>

Atekwana, E. A., & Slater, L. D. (2009). Biogeophysics: A new frontier in Earth science research. *Reviews of Geophysics*, 47(4), L12505. <https://doi.org/10.1029/2009RG000285>

Bate, B., Cao, J., Yang, Y., Cao, J., Zhang, C., & Zhang, S. (2023). Investigation of Cu Adsorption and Migration with Spectral Induced Polarization in Activated Carbon. *Toxics*, 11(3), 221. <https://doi.org/10.3390/toxics11030221>

Ben Moshe, S., & Furman, A. (2022). Real-time monitoring of organic contaminant adsorption in activated carbon filters using spectral induced polarization. *Water Research*, 212, 118103. <https://doi.org/10.1016/j.watres.2022.118103>

Ben Moshe, S., Kessouri, P., Erlich, D., & Furman, A. (2021). Geophysically based analysis of breakthrough curves and ion exchange processes in soil. *Hydrology and Earth System Sciences*, 25(6), 3041–3052. <https://doi.org/10.5194/hess-25-3041-2021>

Binley, A., & Slater, L. D. (2020). Resistivity and Induced Polarization. Cambridge University Press. <https://doi.org/10.1017/9781108685955>

Bücker, M., Flores Orozco, A., Undorf, S., & Kemna, A. (2019). On the Role of Stern- and Diffuse-Layer Polarization Mechanisms in Porous Media. *Journal of Geophysical Research: Solid Earth*, 124(6), 5656–5677. <https://doi.org/10.1029/2019JB017679>

Byrne, G. D., & Hindmarsh, A. C. (1975). A polyalgorithm for the numerical solution of ordinary differential equations. *ACM Transactions on Mathematical Software*, 1(1), 71–96. <https://doi.org/10.1145/355626.355636>

Flores Orozco, A., Williams, K. H., & Kemna, A. (2013). Time-lapse spectral induced polarization imaging of stimulated uranium bioremediation. *Near Surface Geophysics*, 11(5), 531–544. <https://doi.org/10.3997/1873-0604.2013020>

Hao, N., Moysey, S. M. J., Powell, B. A., & Ntarlagiannis, D. (2015). Evaluation of Surface Sorption Processes Using Spectral Induced Polarization and a (22)Na Tracer. *Environmental Science & Technology*, 49(16), 9866–9873. <https://doi.org/10.1021/acs.est.5b01327>

Himes, F. L., & Barber, S. A. (1957). Chelating Ability of Soil Organic Matter. *Soil Science Society of America Journal*, 21(4), 368–373. <https://doi.org/10.2136/sssaj1957.03615995002100040005x>

Hindmarsh, A. C., Brown, P. N., Grant, K. E., Lee, S. L., Serban, R., Shumaker, D. E., & Woodward, C. S. (2005). SUNDIALS: suite of nonlinear and differential/algebraic equation solvers. *ACM Transactions on Mathematical Software (TOMS)*, 31(3), 363–396. <https://doi.org/10.1145/1089014.1089020>

Huang, W., Peng, P., Yu, Z., & Fu, J. (2003). Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Applied Geochemistry*, 18(7), 955–972. [https://doi.org/10.1016/S0883-2927\(02\)00205-6](https://doi.org/10.1016/S0883-2927(02)00205-6)

Jackson, K. R., & Sacks-Davis, R. (1980). An alternative implementation of variable step-size multistep formulas for stiff ODEs. *ACM Transactions on Mathematical Software*, 6(3), 295–318. <https://doi.org/10.1145/355900.355903>

Katona, T., Gilfedder, B. S., Frei, S., Bucker, M., & Flores Orozco, A. (2021). High-resolution induced polarization imaging of biogeochemical carbon-turnover hot spots in a peatland. *Biogeosciences*, 18(13), 4039–4058.

Kessouri, P., Furman, A., Huisman, J. A., Martin, T., Mellage, A., Ntarlagiannis, D., Bucker, M., Ehosioka, S., Fernandez, P., Flores Orozco, A., Kemna, A., Nguyen, F., Pilawski, T., Saneiyan, S., Schmutz, M., Schwartz, N., Weigand, M., Wu, Y., Zhang, C., & Placencia-Gomez, E. (2019). Induced polarization applied to biogeophysics: Recent advances and future prospects. *Near Surface Geophysics*, 17(6), 595–621. <https://doi.org/10.1002/nsg.12072>

Kumar, R., Carroll, C., Hartikainen, A., & Martin, O. (2019). ArviZ a unified library for exploratory analysis of Bayesian models in Python. *Journal of Open Source Software*, 4(33), 1143. <https://doi.org/10.21105/joss.01143>

Lair, G. J., Gerzabek, M. H., & Haberhauer, G. (2007). Sorption of heavy metals on organic and inorganic soil constituents. *Environmental Chemistry Letters*, 5(1), 23–27. <https://doi.org/10.1007/s10311-006-0059-9>

Leroy, P., Revil, A., Kemna, A., Cosenza, P., & Ghorbani, A. (2008). Complex conductivity of water-saturated packs of glass beads. *Journal of Colloid and Interface Science*, 321(1), 103–117. <https://doi.org/10.1016/j.jcis.2007.12.031>

Li, L., Sullivan, P. L., Benettin, P., Cirpka, O. A., Bishop, K., Brantley, S. L., Knapp, J. L. A., Meerveld, I., Rinaldo, A., Seibert, J., Wen, H., & Kirchner, J. W. (2021). Toward catchment hydro-biogeochemical theories. *WIREs Water*, 8(1), e1495. <https://doi.org/10.1002/wat2.1495>

Marshall, D. J., & Madden, T. R. (1959). Induced polarization, a study of its causes. *Geophysics*, 24(4), 790–816. <https://doi.org/10.1190/1.1438659>

Mellage, A., Dörrich, M., & Haderlein, S. B. (2022). Capturing In Situ Glyphosate (De)sorption Kinetics in Floodplain Aquifer Sediment Columns: Geophysical Measurements and Reactive Transport Modeling. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.1c07119>

Mellage, A., Smeaton, C. M., Furman, A., Atekwana, E. A., Rezanezhad, F., & Van Cappellen, P. (2018). Linking Spectral Induced Polarization (SIP) and Subsurface Microbial Processes: Results from Sand Column Incubation Experiments. *Environmental Science & Technology*, 52(4), 2081–2090. <https://doi.org/10.1021/acs.est.7b04420>

Mellage, A., Zakai, G., Efrati, B., Pagel, H., & Schwartz, N. (2022). Paraquat sorption- and organic matter-induced modifications of soil spectral induced polarization (SIP) signals. *Geophysical Journal International*, 229(2), 1422–1433. <https://doi.org/10.1093/gji/ggab531>

Patterson, J. W., Allen, H. E., & Scala, J. J. (1977). Carbonate precipitation for heavy metals pollutants. *Journal (Water Pollution Control Federation)*, 2397–2410.

Randhawa, N. S., & Broadbent, F. E. (1965). SOIL ORGANIC MATTER-METAL COMPLEXES: 5. REACTIONS OF ZINC WITH MODEL COMPOUNDS AND HUMIC ACID. *Soil Science*, 99(5). https://journals.lww.com/soilsci/fulltext/1965/05000/soil_organic_matter_metal_complexes__5__reactions.2.aspx

Revil, A., Cathles, L. M., Losh, S., & Nunn, J. A. (1998). Electrical conductivity in shaly sands with geophysical applications. *Journal of Geophysical Research: Solid Earth*, 103(B10), 23925–23936. <https://doi.org/10.1029/98JB02125>

Rühlmann, J., Körschens, M., & Graefe, J. (2006). A new approach to calculate the particle density of soils considering properties of the soil organic matter and the mineral matrix. *Geoderma*, 130(3), 272–283. <https://doi.org/10.1016/j.geoderma.2005.01.024>

Saneiyan, S. (2019). *Geophysical methods for monitoring soil stabilization by microbial induced carbonate precipitation* [Doctoral thesis, Rutgers University]. <https://doi.org/10.7282/t3-scpk-bd54>

Scheidegger, A. E. (1961). General theory of dispersion in porous media. *Journal of Geophysical Research* (1896-1977), 66(10), 3273–3278. <https://doi.org/10.1029/JZ066i010p03273>

Schwartz, N., & Furman, A. (2014). On the spectral induced polarization signature of soil organic matter. *Geophysical Journal International*, 200(1), 589–595. <https://doi.org/10.1093/gji/ggu410>

Schwarz, G. (1962). A THEORY OF THE LOW-FREQUENCY DIELECTRIC DISPERSION OF COLLOIDAL PARTICLES IN ELECTROLYTE SOLUTION 1,2. *The Journal of Physical Chemistry*, 66(12), 2636–2642. <https://doi.org/10.1021/j100818a067>

Serban, R., & Hindmarsh, A. C. (2008). *CVODES: The sensitivity-enabled ODE solver in SUNDIALS*. 257–269. <https://doi.org/10.1115/DETC2005-85597>

Seyboldt, A., Osthege, M., Störko, A., Widmer, L., Mares, B., & Porter, J. R. (2024). *pymc-devs/sunode: V0.6.0* [Computer software]. Zenodo. <https://zenodo.org/records/11187750>

Slater, L. D., & Glaser, D. R. (2003). Controls on induced polarization in sandy unconsolidated sediments and application to aquifer characterization. *Geophysics*, 68(5), 1547–1558. <https://doi.org/10.1190/1.1620628>

Strobel, C. (2024). *Electronic appendix for “Are we there yet? A critical experimental assessment of the application of induced polarization for monitoring geochemical processes”*, Strobel, C., Störko, A., Olaf, O.A. & Melage, A. (0.0) [Dataset]. Zenodo. <https://doi.org/10.5281/ZENODO.12788754>

Strobel, C., Abramov, S., Huisman, J. A., Cirpka, O. A., & Melage, A. (2023). Spectral Induced Polarization (SIP) of Denitrification-Driven Microbial Activity in Column Experiments

Packed With Calcareous Aquifer Sediments. *Journal of Geophysical Research: Biogeosciences*,
128(1). <https://doi.org/10.1029/2022JG007190>

Strobel, C., Doerrich, M., Stieff, E. -H., Huisman, J. A., Cirpka, O. A., & Melling, A.
(2023). Organic Matter Matters—The Imaginary Conductivity of Sediments Rich in Solid
Organic Carbon. *Geophysical Research Letters*, 50(23), e2023GL104630.
<https://doi.org/10.1029/2023GL104630>

Tsukanov, K., & Schwartz, N. (2020). Relationship between wheat root properties and its
electrical signature using the spectral induced polarization method. *Vadose Zone Journal*, 19(1),
e20014. <https://doi.org/10.1002/vzj2.20014>

Vaudelet, P., Revil, A., Schmutz, M., Franceschi, M., & Bégassat, P. (2011). Induced
polarization signatures of cations exhibiting differential sorption behaviors in saturated sands.
Water Resources Research, 47(2). <https://doi.org/10.1029/2010WR009310>

Vehtari, A., Gelman, A., Simpson, D., Carpenter, B., & Bürkner, P.-C. (2021). Rank-
normalization, folding, and localization: An improved $\{\widehat{R}\}$ for assessing
convergence of MCMC. *Bayesian Analysis*, 16(2), 667–718. <https://doi.org/10.1214/20-BA1221>

Weigand, M., & Kemna, A. (2019). Imaging and functional characterization of crop root
systems using spectroscopic electrical impedance measurements. *Plant and Soil*, 435(1–2), 201–
224. <https://doi.org/10.1007/s11104-018-3867-3>

Weller, A., Breede, K., Slater, L., & Nordsiek, S. (2011). Effect of changing water salinity
on complex conductivity spectra of sandstones. *GEOPHYSICS*, 76(5), F315–F327.
<https://doi.org/10.1190/geo2011-0072.1>

Zhang, C., Revil, A., Fujita, Y., Munakata-Marr, J., & Redden, G. (2014). Quadrature
conductivity: A quantitative indicator of bacterial abundance in porous media. *Geophysics*,
79(6), D363–D375. <https://doi.org/10.1190/geo2014-0107.1>

References in the Supporting Information

755 Bromly M., Hinz C. and Aylmore L. A. G. (2007) Relation of dispersivity to properties of
756 homogeneous saturated repacked soil columns. *European J Soil Science* 58, 293–301.

757 Strobel C., Abramov S., Huisman J. A., Cirpka O. A. and Melling A. (2023) Spectral
758 Induced Polarization (SIP) of Denitrification-Driven Microbial Activity in Column Experiments
759 Packed With Calcareous Aquifer Sediments. *J. Geophys. Res. Biogeosci.* 128.

760

A.3.1. Publication 3: supporting information



Water resources research

Supporting Information for

Are we there yet? A critical experimental assessment of the application of induced polarization for monitoring geochemical processes

C. Strobel^{1,2*}, A. Störiko³, O.A. Cirpka¹ and A. Mellage²

¹Department of Geosciences, University of Tübingen, Tübingen, Germany

²Civil and Environmental Engineering, University of Kassel, Kassel, Germany

³Department of Water Management, Delft University of Technology, Delft, Netherlands

*Corresponding author: Cora Strobel, University of Tübingen, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany;
(cora.strobel@uni-tuebingen.de)

Secondary corresponding author: Adrian Mellage (adrian.mellage@uni-kassel.de)

Contents of this file

Figures S1 to S17

Tables S1 to S3

Introduction

The supplementary material contains detailed information on the Bayesian parameter estimation as well as figures showing the results of the experimental columns that could not be shown within the main manuscript. In addition, modelling results of the NaBr and CaBr₂ experiments and of parameter estimation scenarios that could not be shown in the main manuscript are presented here.

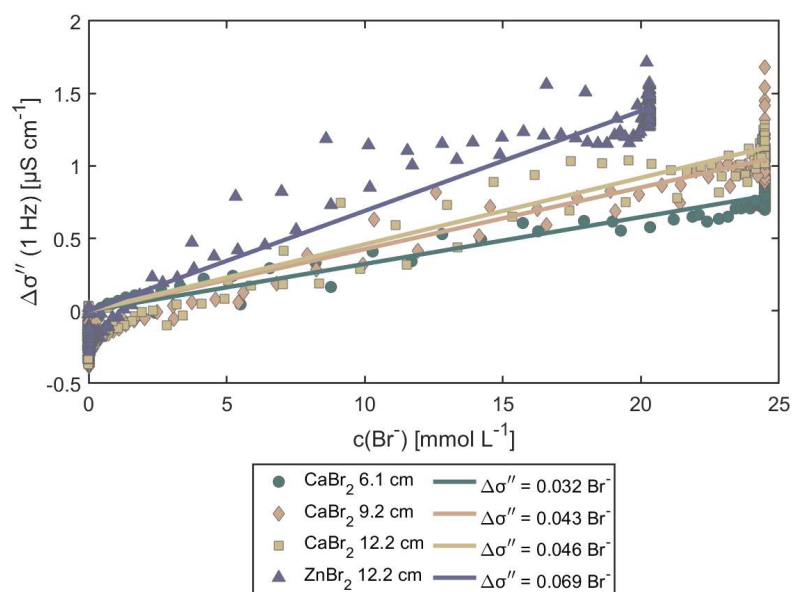


Figure S1: Comparison of the change in σ'' with the simulated Br^- concentration at the electrodes' midpoints for experimental phases in which we assume only minor changes in surface chemistry.

Qualitative interpretation of SIP data

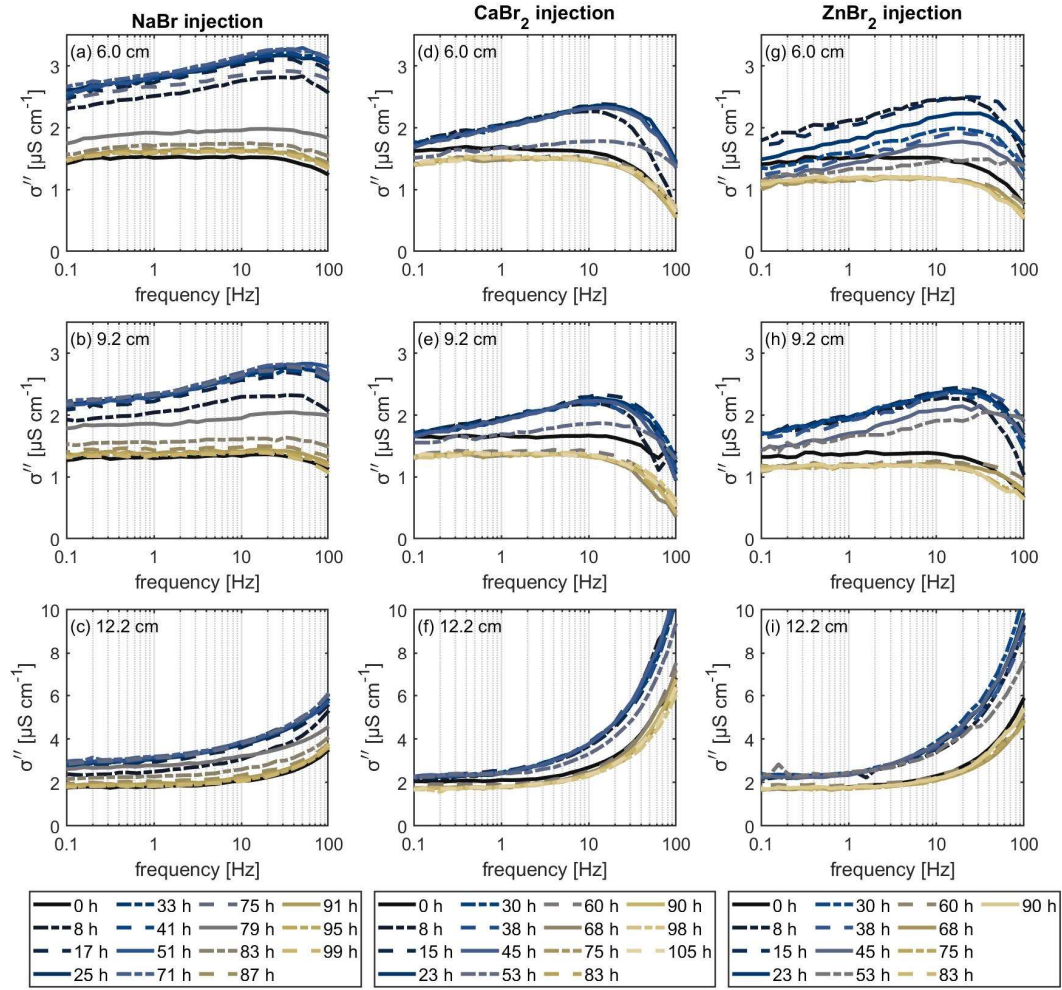


Figure S2: σ'' spectra of column OM01 during the NaBr injection (a – c), the CaBr_2 injection (d – f) and the ZnBr_2 injection (g – i). Flow was from top to bottom, distances denote the distance from the injection point.

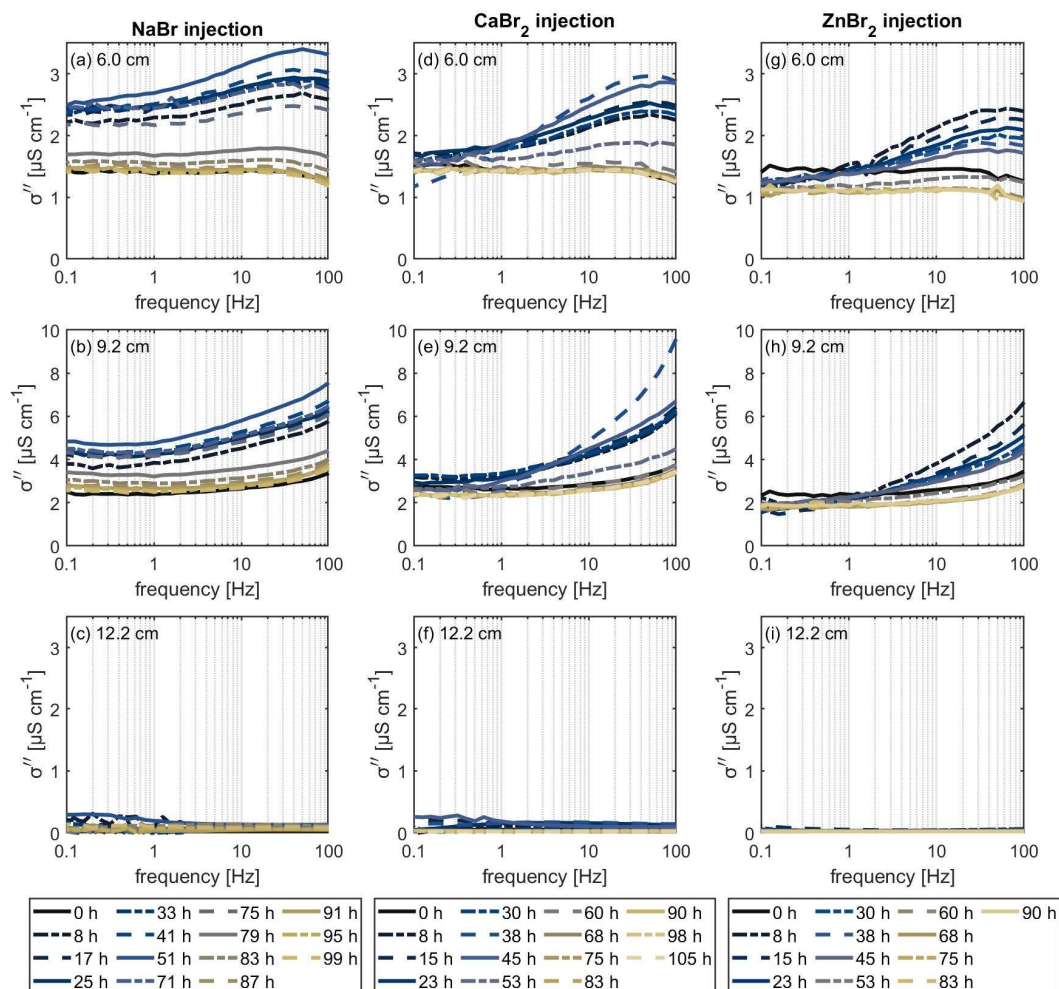


Figure S3: σ'' spectra of column OM02 during the NaBr injection (a – c), the CaBr₂ injection (d – f) and the ZnBr₂ injection (g – i). Flow was from top to bottom, distances denote the distance from the injection point. Note that the lowest electrode was in bad contact with the column and the data at 12.2 cm can thus be ignored.

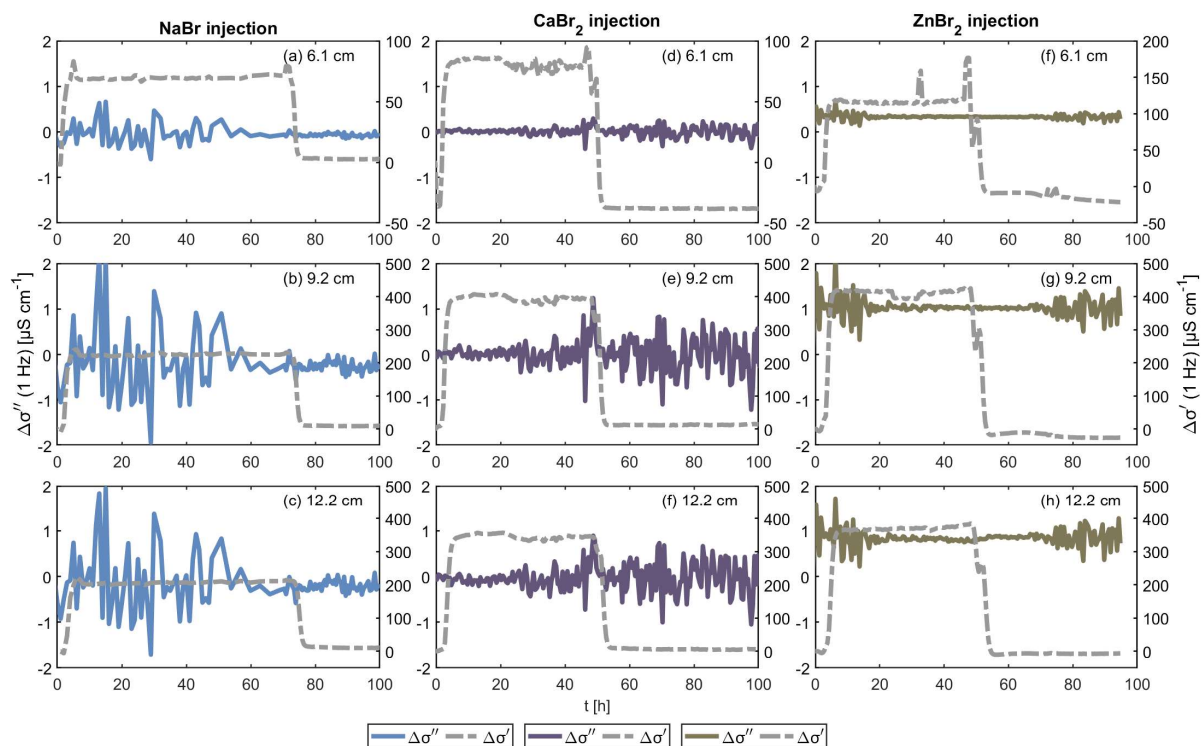


Figure S4: Comparison of the change in real and imaginary conductivity during the three cation injections: the NaBr injection (a – c), the CaBr_2 injection (d – f) and the ZnBr_2 injection (f – h). In each case all three SIP-measurement locations are shown for column S01. Flow was from top to bottom, distances denote the distance from the injection point.

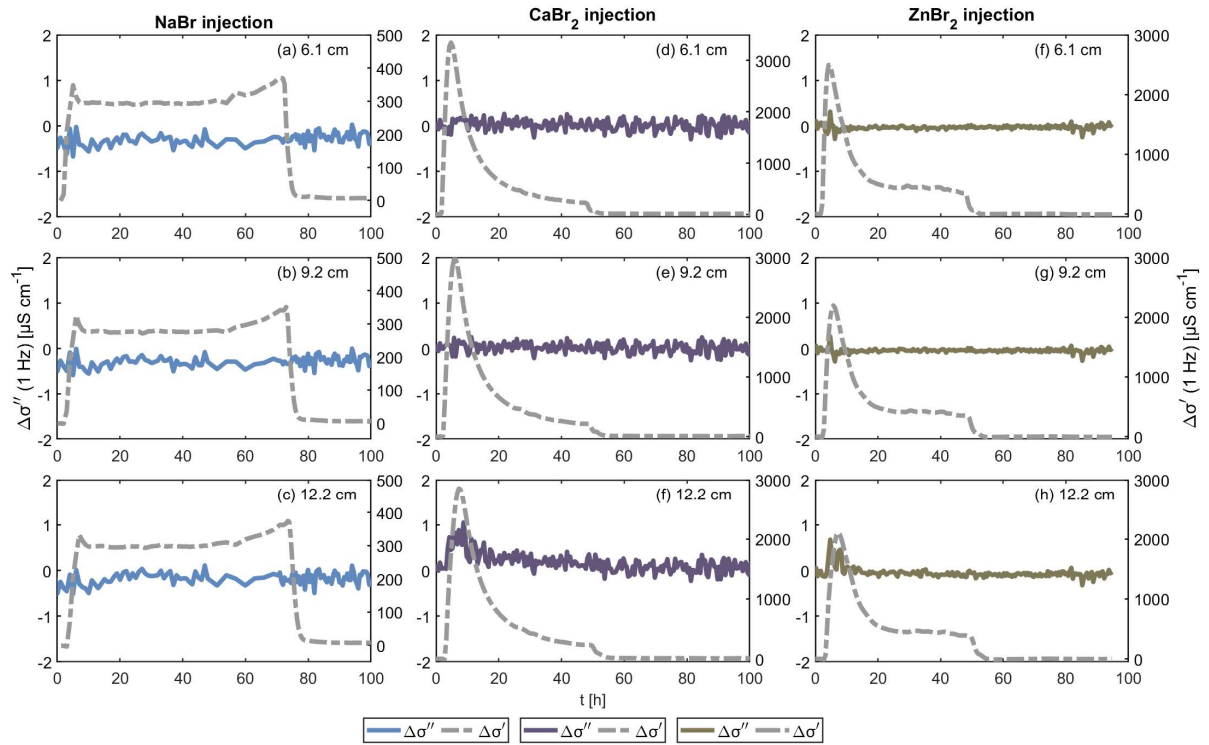


Figure S5: Comparison of the change in real and imaginary conductivity during the three cation injections: the NaBr injection (a – c), the CaBr₂ injection (d – f) and the ZnBr₂ injection (f – h). In each case all three SIP-measurement locations are shown for column S02. Flow was from top to bottom, distances denote the distance from the injection point.

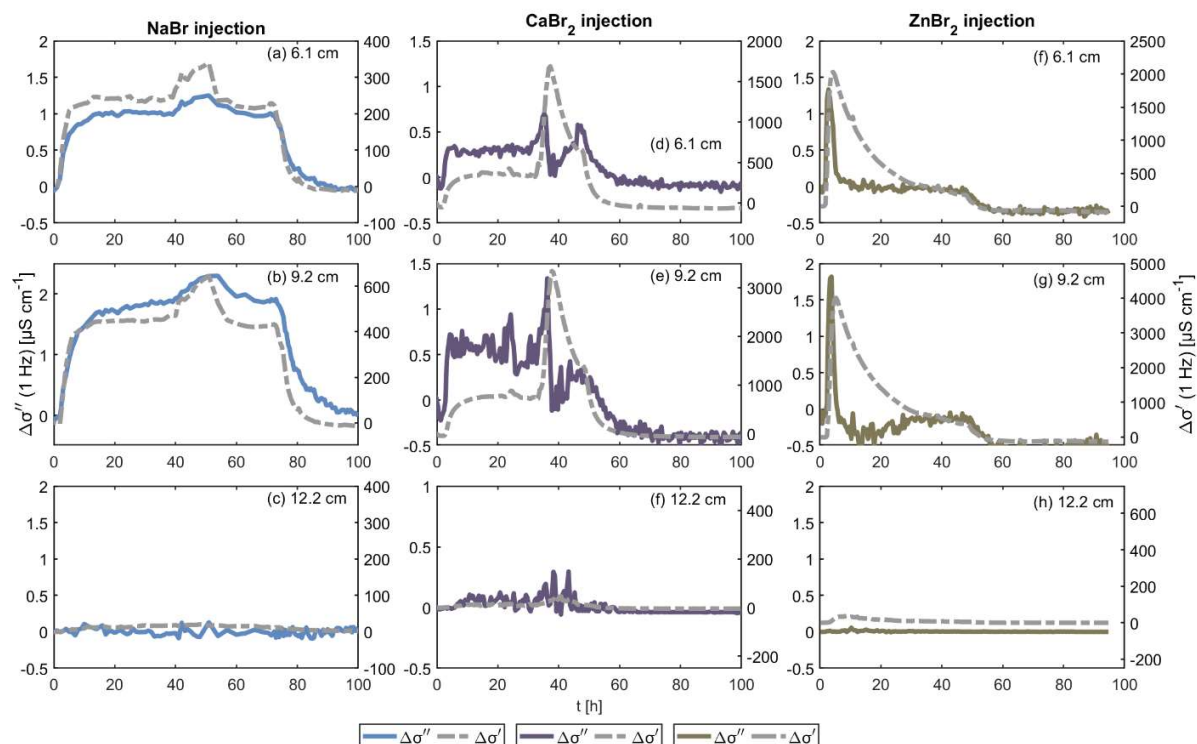


Figure S6: Comparison of the change in real and imaginary conductivity during the three cation injections: the NaBr injection (a – c), the CaBr_2 injection (d – f) and the ZnBr_2 injection (f – h). In each case all three SIP-measurement locations are shown for column OM02. Flow was from top to bottom, distances denote the distance from the injection point. Note that the lowest electrode was in bad contact with the column and the data at 12.2 cm can thus be ignored.

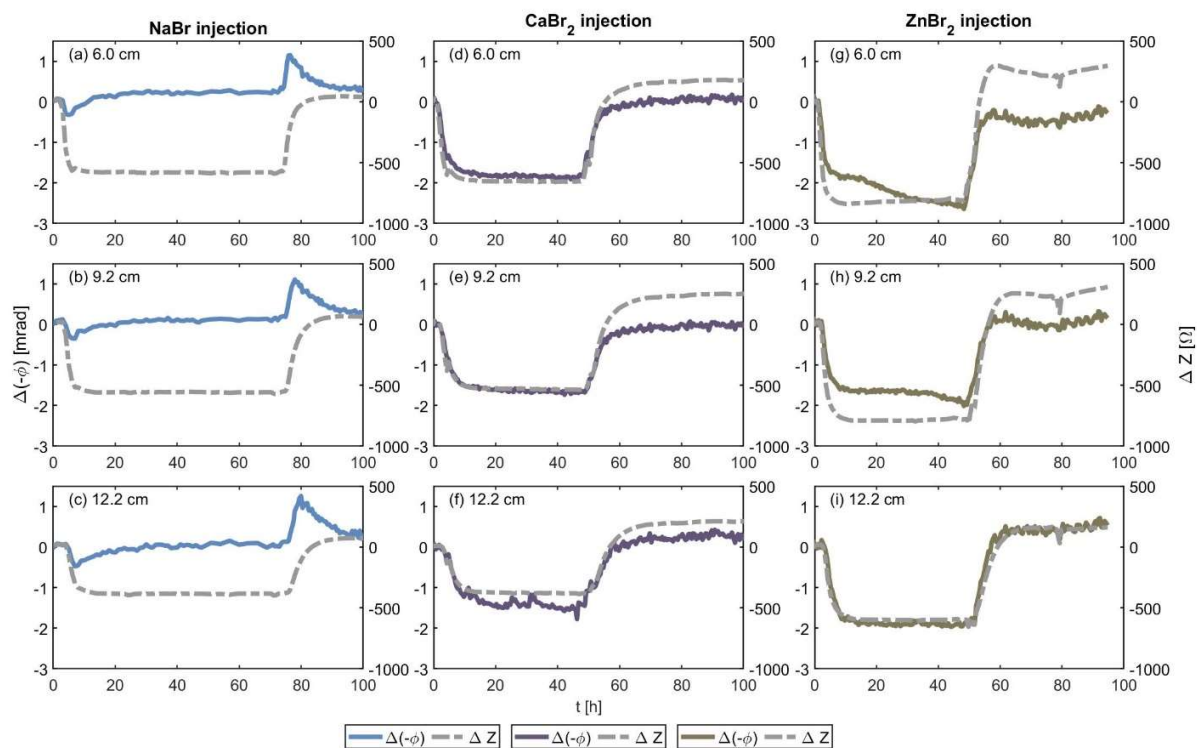


Figure S7: The change in phase shift and impedance during the NaBr injection (a – c), the CaBr₂ injection (d – f) and the ZnBr₂ injection (g – i) in column OM01.

Geochemical data of columns not shown in the main manuscript

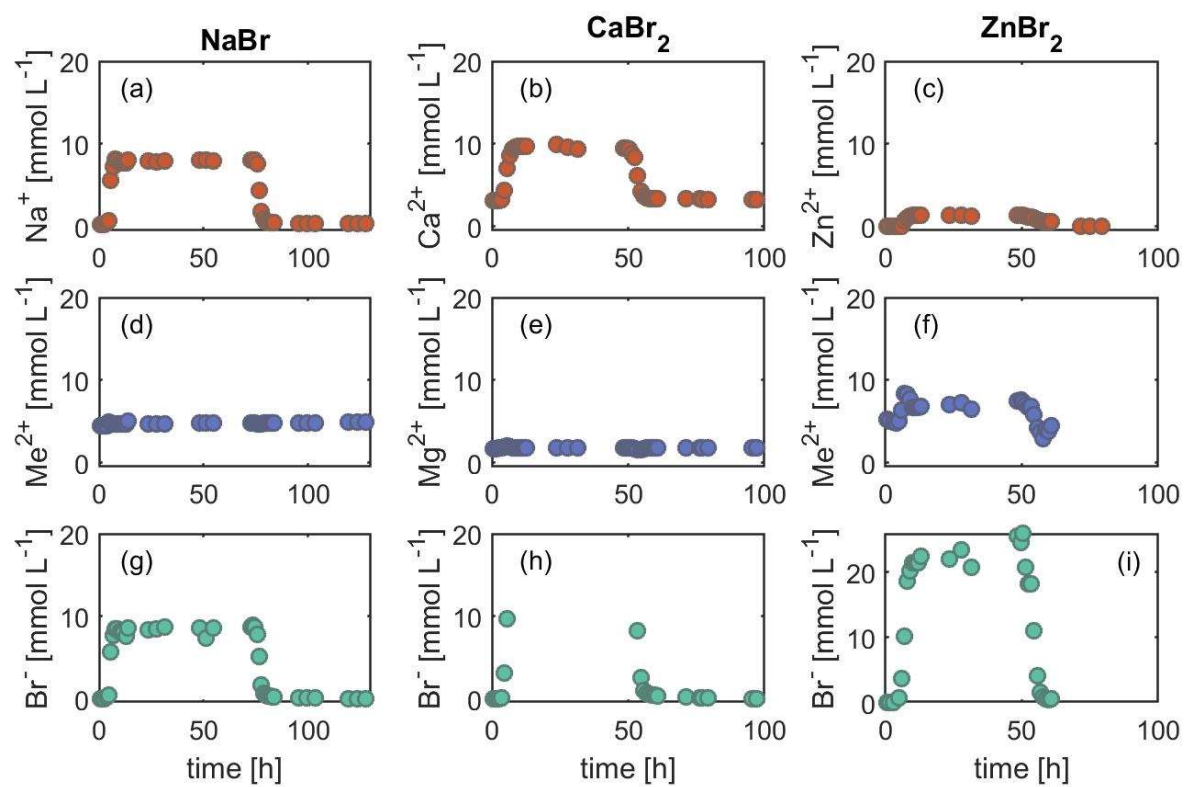


Figure S8: Outflow concentration data of column S01 for all experiments.

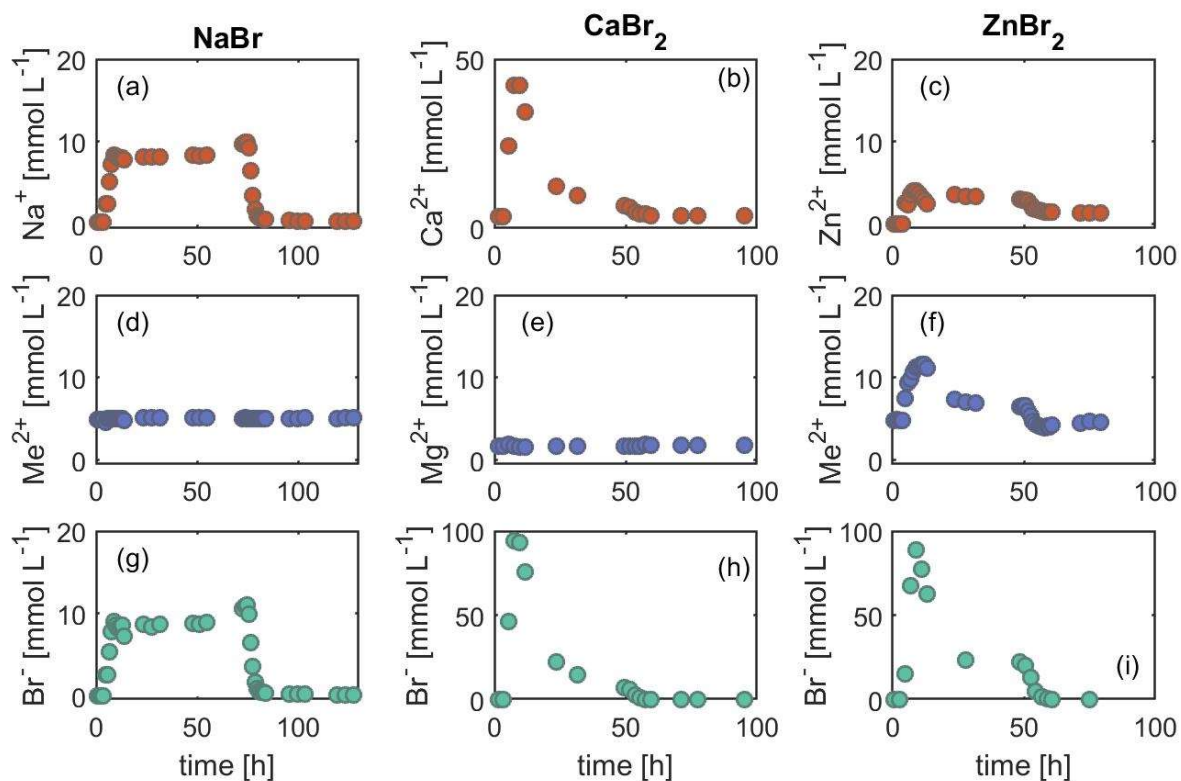


Figure S9: Outflow concentration data of column S02 for all experiments.

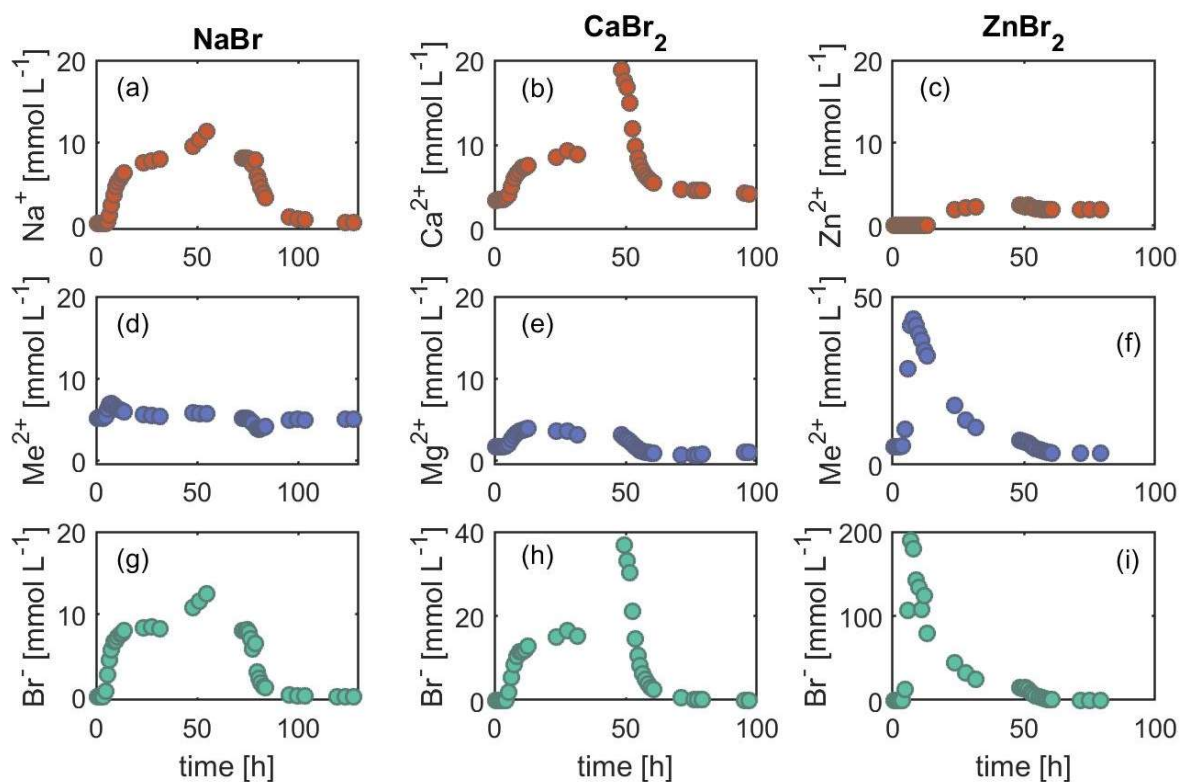


Figure S10: Outflow concentration data of column OM02 for all experiments.

Reactive transport model

Model parameters

Table S1: Parameters that were set to fixed values in the simulation.

parameter	symbol	value	units
diffusion coefficient	D	1e-09	m ² /s
flow rate in Na ⁺ -experiment	Q	11.9	mL/hr
flow rate in Ca ²⁺ -experiment	Q	11.5	mL/hr
flow rate in Zn ²⁺ -experiment	Q	11.3	mL/hr
column length	l	0.18	m
column radius	r	1.75	cm
x-spacing	Δx	0.001	m
solid density	ρ_s	2.46	g/cm ³
initial concentration of Br ⁻ (all experiments)		0	mmol/L
initial concentration of Na ⁺ in Na-experiment		0	mmol/L
initial concentration of Me ²⁺ in Na-experiment		5.1	mmol/L
initial concentration of Ca ²⁺ in Ca-experiment		3.4	mmol/L
initial concentration of Mg ²⁺ in Ca-experiment		1.8	mmol/L
initial concentration of Zn ²⁺ in Zn-experiment		0	mmol/L
initial concentration of Me ²⁺ in Zn-experiment		5.1	mmol/L
inflow concentration of Br ⁻ in Na-experiment		8.8	mmol/L
inflow concentration of Na ⁺ in Na-experiment		8.8	mmol/L
inflow concentration of Me ²⁺ in Na-experiment		5.1	mmol/L
inflow concentration of Br ⁻ in Ca-experiment		16	mmol/L
inflow concentration of Ca ²⁺ in Ca-experiment		11.4	mmol/L
inflow concentration of Mg ²⁺ in Ca-experiment		1.8	mmol/L
inflow concentration of Zn ²⁺ in Zn-experiment		10.2	mmol/L
inflow concentration of Me ²⁺ in Zn-experiment		5.1	mmol/L
standard deviation of SIP data		0.2	μS/cm
standard deviation of Br ⁻ breakthrough curve		1	mmol/L
standard deviation of cation breakthrough curve		0.5	mmol/L

Table S2: Prior distributions of parameters estimated in the Bayesian framework. The distributions are parameterized in terms of a mean and standard deviation (sd). For log-normal distributions, the mean and standard deviation of the underlying normal distribution are given.

parameter	symbol	units	distribution	mean	sd	reference
porosity	n_e	dimensionless	beta	0.7	0.1	(Strobel et al., 2023)
dispersivity	α	m	log-normal	$\ln(0.005)$	0.5	(Bromly et al., 2007; Strobel et al., 2023)
sorption half-saturation constant of Na^+	K_{Na^+}	mmol/L	log-normal	$\ln(0.5)$	1	
sorption half-saturation constant of Ca^{2+}	$K_{\text{Ca}^{2+}}$	mmol/L	log-normal	$\ln(0.05)$	1	
sorption half-saturation constant of Mg^{2+}	$K_{\text{Mg}^{2+}}$	mmol/L	log-normal	$\ln(0.05)$	1	
sorption half-saturation constant of Me^{2+}	$K_{\text{Me}^{2+}}$	mmol/L	log-normal	$\ln(0.05)$	1	
sorption half-saturation constant of Zn^{2+}	$K_{\text{Zn}^{2+}}$	mmol/L	log-normal	$\ln(0.01)$	1	
sorption site density	s_{max}	mmol/g	log-normal	$\ln(0.12)$	0.5	measured cation exchange capacity
kinetic desorption rate constant	k_{desorb}	1/s	log-normal	$\ln(0.0005)$	2	
Zn precipitation rate constant	k_{precip}	1/s	log-normal	$\ln(0.5/3600)$	1	
Br^- inflow concentration in the Zn experiment	$c_{\text{in}}^{\text{Br}}$	mmol/L	log-normal	$\ln(20.3)$	0.05	measurement in the inflow
proportionality constant of sorbed concentrations for $\Delta\sigma''$	p	$\mu\text{S g}/(\text{cm mmol})$	normal	0	300	
proportionality constant of Br^- concentrations for $\Delta\sigma''$	a	$\mu\text{S L} / (\text{cm mmol})$	log-normal	$\ln(0.05)$	1	

Fitting results for Na⁺ and Ca²⁺ injections and all scenarios

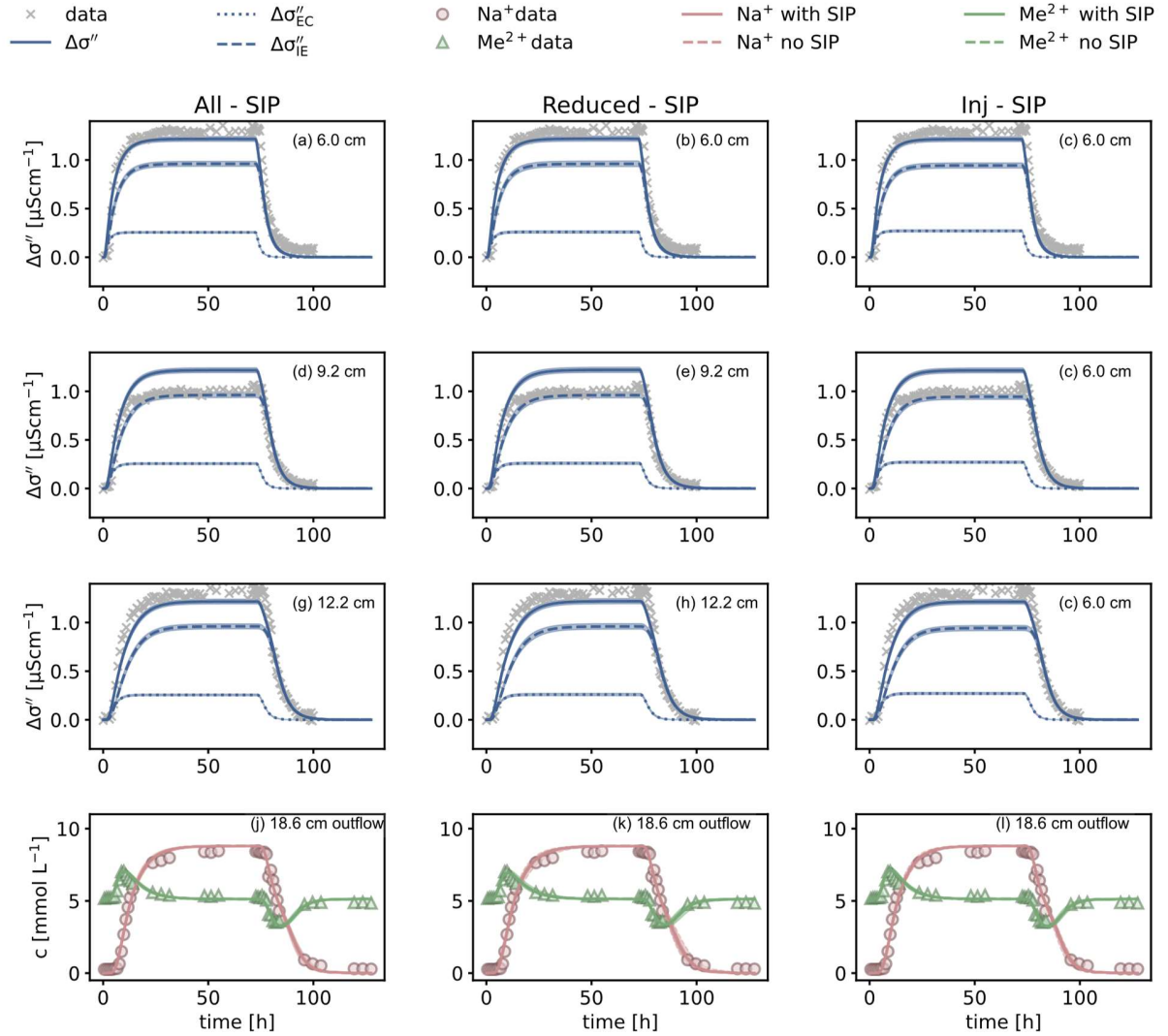


Figure S11: Comparison of the simulation of the NaBr experiment using either all chemistry data available (left column), using every third datapoint (centered column) or only the concentrations of Na⁺ (right column). Panels a – f show the comparison of the simulated $\Delta\sigma''$ with $\Delta\sigma''$ at all measurement locations.

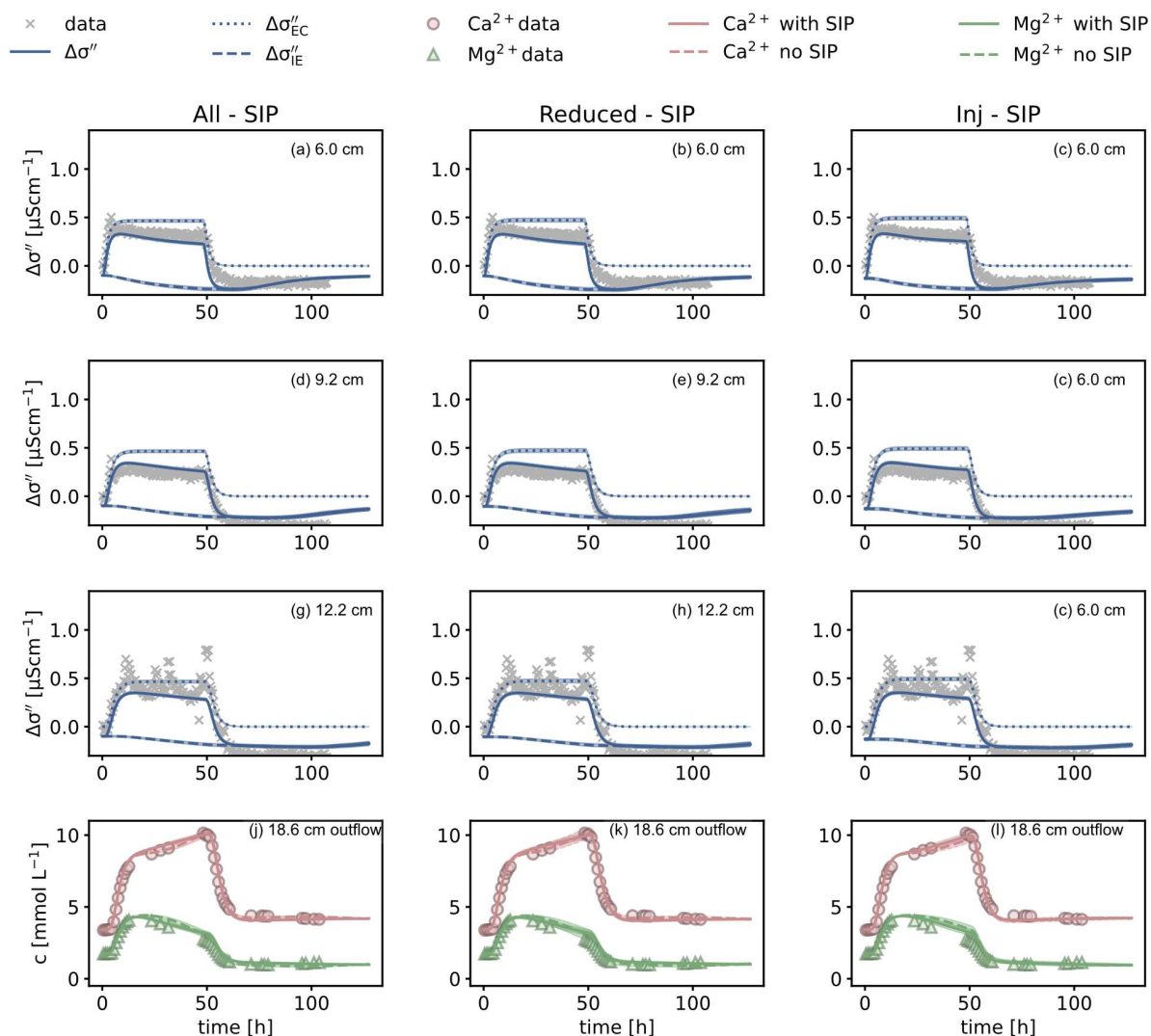


Figure S12: Comparison of the simulation of the CaBr₂ experiment using either all chemistry data available (left column), using every third datapoint (centered column) or only the concentrations of Ca²⁺ (right column). Panels a – f show the comparison of the simulated $\Delta\sigma''$ with $\Delta\sigma''$ at all measurement locations.

Fitting results and sorption profiles for Zn^{2+} injection and all scenarios

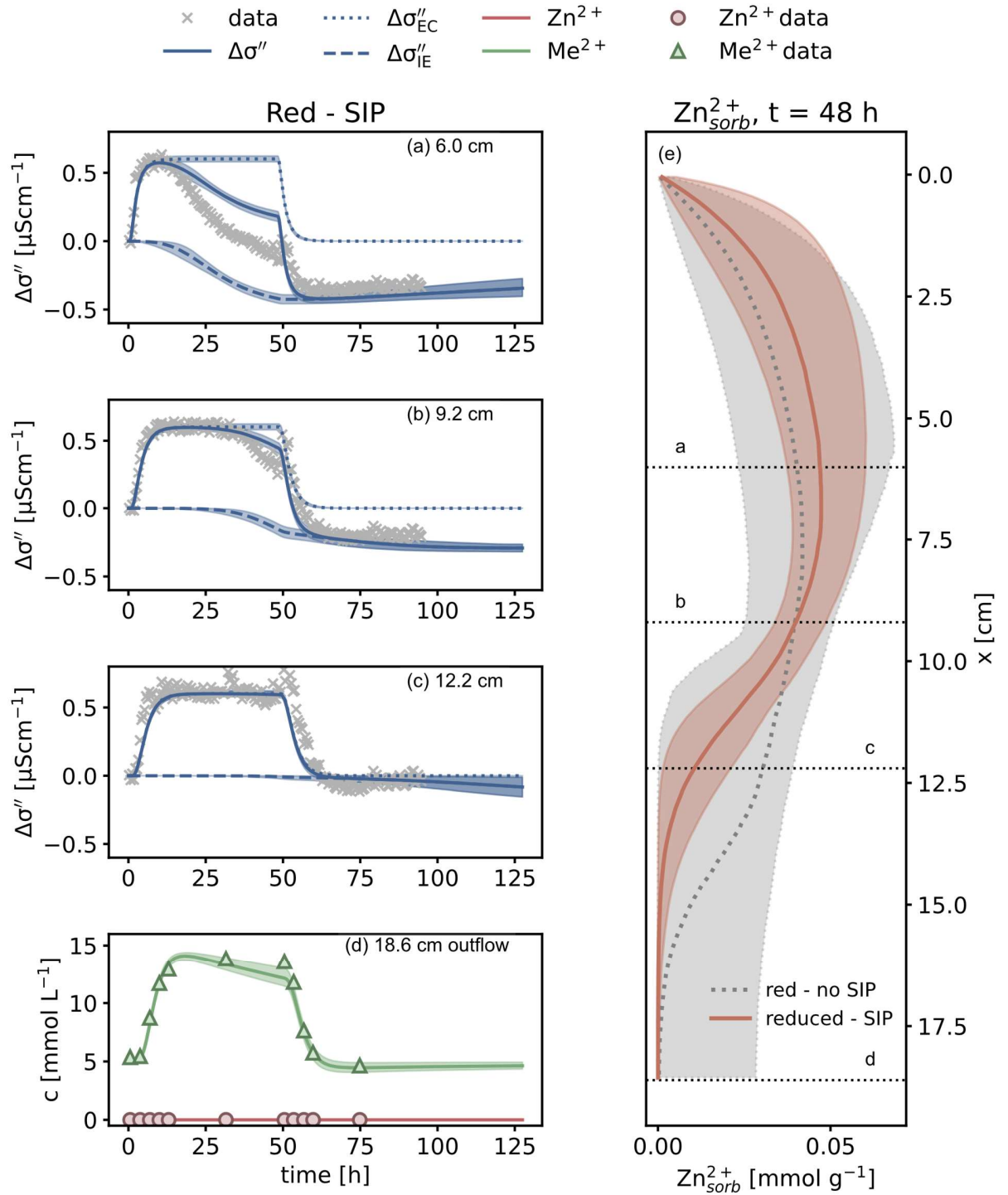


Figure S13: Model-data comparison of the simulation of the Zn^{2+} -experiment using a reduced concentration dataset (left column). Panels a – c show the comparison of the simulated $\Delta\sigma''$ compared to measured $\Delta\sigma''$ at all locations. In addition, the contribution of electrical conductivity, $\Delta\sigma''_{\text{EC}}$, and the ion exchange reaction, $\Delta\sigma''_{\text{IE}}$, to the overall change in σ'' are shown as

dotted and dashed lines, respectively. In panel d the simulated concentrations are compared with the measured concentrations. Additionally, a profile of the simulated sorbed concentrations of Zn^{2+} at the end of the injection is shown for scenario with and without the SIP data (e). The dashed lines in panel denote the location of the SIP measurements and the outflow. The shaded areas show the range between the 5th and 95th quantile.

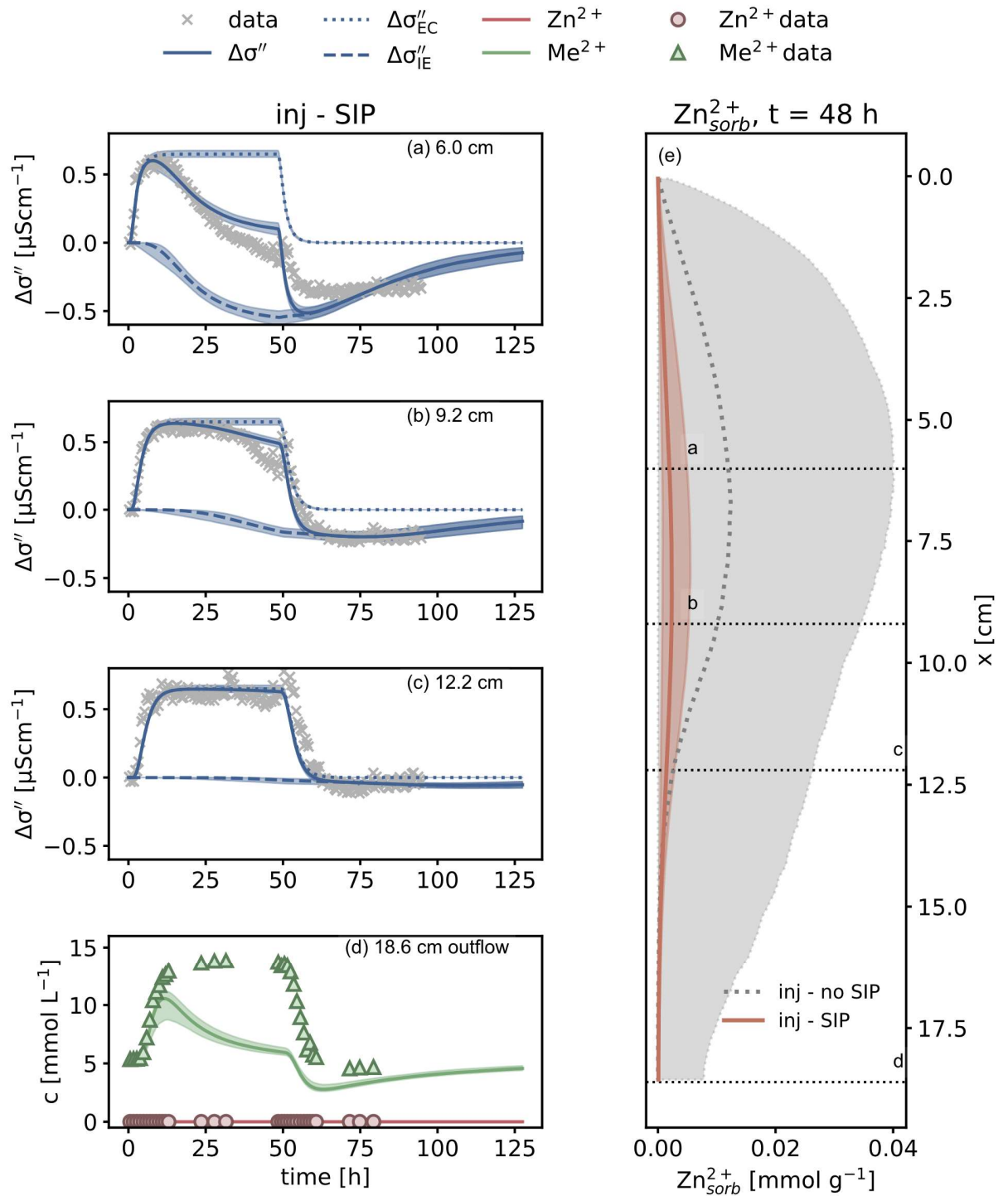


Figure S14: Model-data comparison of the simulation of the Zn^{2+} -experiment using only the Zn^{2+} data (left column). Panels a – c show the comparison of the simulated $\Delta\sigma''$ compared to measured $\Delta\sigma''$ at all locations. In addition, the contribution of electrical conductivity, $\Delta\sigma''_{\text{EC}}$, and the ion exchange reaction, $\Delta\sigma''_{\text{IE}}$, to the overall change in σ'' are shown as dotted and dashed lines, respectively. In panel d the simulated concentrations are compared with the measured concentrations. Additionally, a profile of the simulated sorbed concentrations of Zn^{2+} at the end of the injection is shown for the scenarios with and without the SIP data (e). The dashed lines in panel

denote the location of the SIP measurements and the outflow. The shaded areas show the range between the 5th and 95th quantile.

Parameter estimates of different scenarios

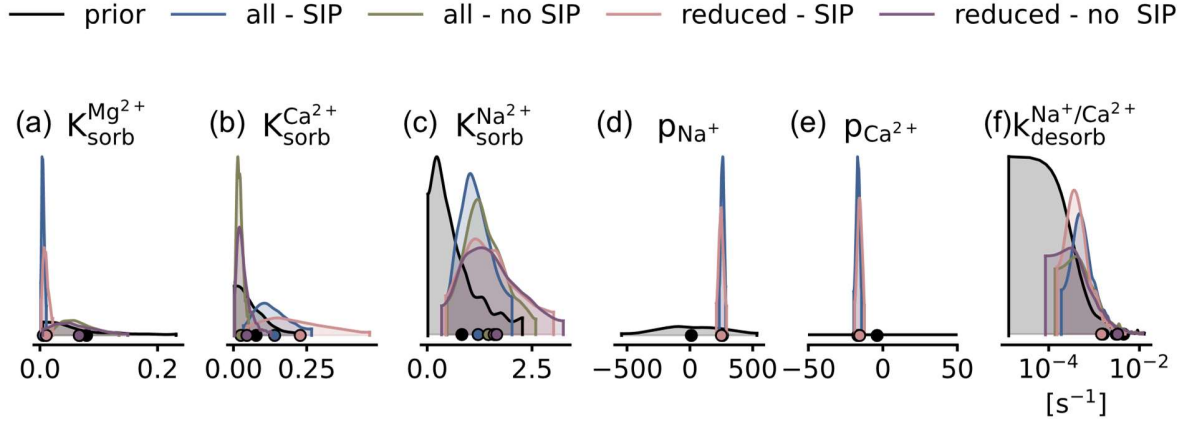


Figure S15: Kernel density estimates of the prior distribution and the posterior distributions of parameters not shown in the main manuscript. The posterior distributions are shown for the different scenarios of input data with or without SIP data and/or background ion concentrations. Plots are cut at the 94 % highest density interval.

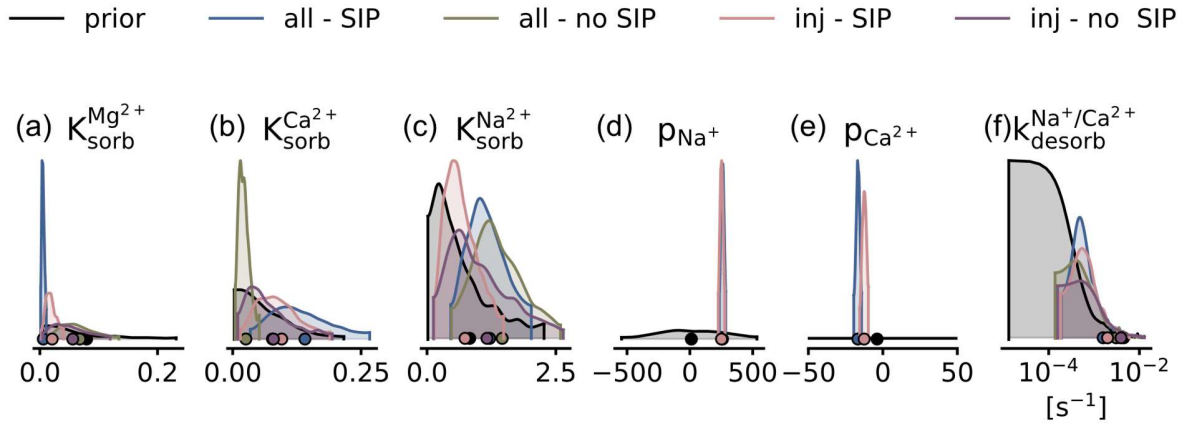


Figure S16: Kernel density estimates of the prior distribution and the posterior distributions of parameters not shown in the main manuscript. The posterior distributions are shown for the different scenarios of input data with or without SIP data and/or background ion concentrations. Plots are cut at the 94 % highest density interval.

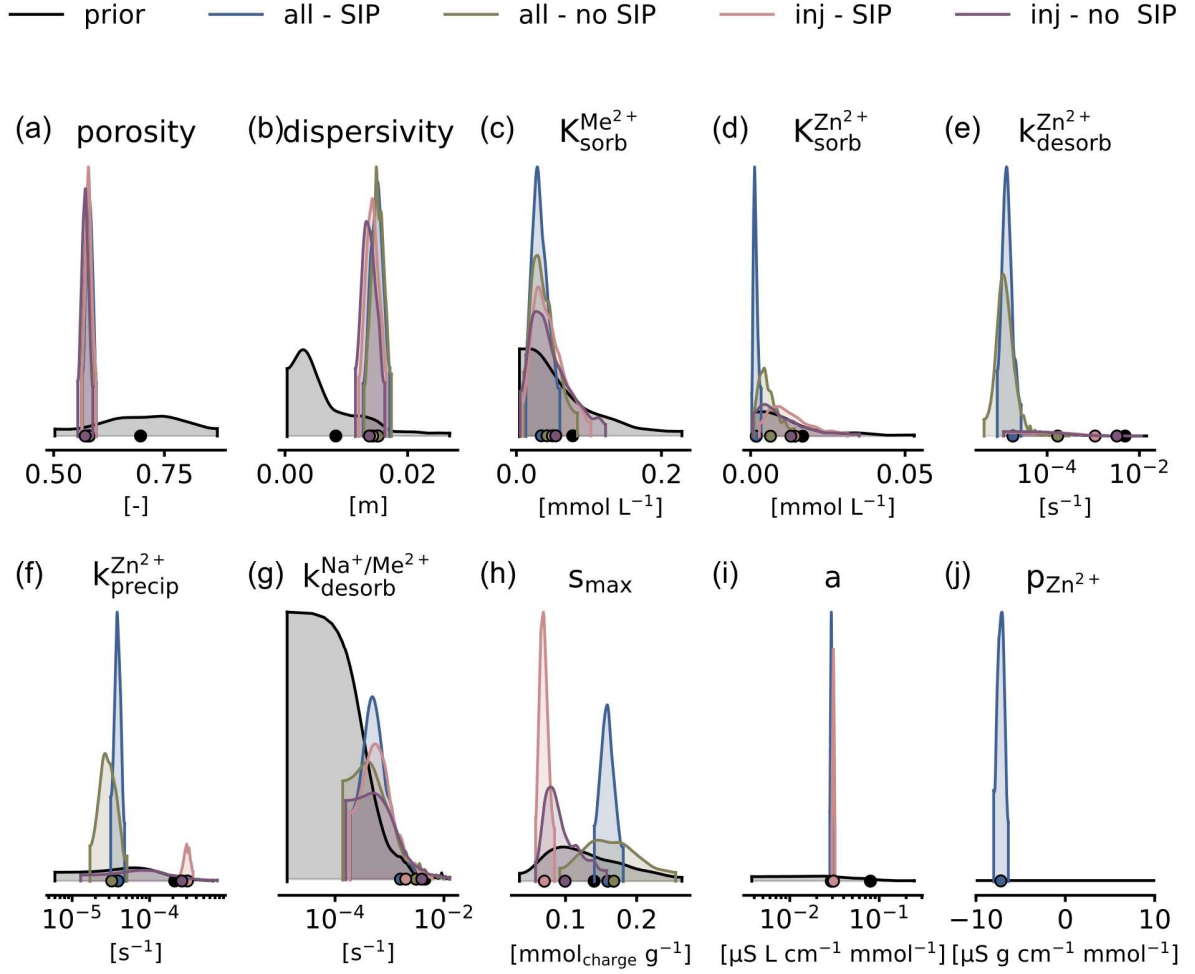


Figure S17: Kernel density estimates of the prior and posterior distributions of parameters relevant for the Zn^{2+} experiment. The posterior distributions are shown for the different scenarios of all concentration data or using only the Zn^{2+} data with or without SIP data. Plots are cut at the 94 % highest density interval.

Table S3: Median values and standard deviations of the estimated parameters from the posterior distribution obtained by the All-SIP scenario that used all available data for the parameter estimation.

parameter	symbol	units	mean	sd
porosity	n_e	dimensionless	0.58	0.008
dispersivity	α	m	0.015	0.001
sorption half-saturation constant of Na^+	K_{Na^+}	mmol/L	1.215	0.444
sorption half-saturation constant of Ca^{2+}	$K_{\text{Ca}^{2+}}$	mmol/L	0.141	0.069
sorption half-saturation constant of Mg^{2+}	$K_{\text{Mg}^{2+}}$	mmol/L	0.006	0.006
sorption half-saturation constant of Me^{2+}	$K_{\text{Me}^{2+}}$	mmol/L	0.032	0.013

sorption half-saturation constant of Zn^{2+}	$K_{Zn^{2+}}$	mmol/L	0.002	0.001
sorption site density	s_{max}	mmol/g	0.159	0.011
kinetic desorption rate constant	k_{desorb}	1/s	Na ⁺ /Ca ²⁺ : 8.37×10^{-4} Zn ²⁺ : 1.46×10^{-5}	Na ⁺ /Ca ²⁺ : 2.9×10^{-3} Zn ²⁺ : 5×10^{-5}
Zn precipitation rate constant	k_{precip}	1/s	3.88×10^{-5}	4.3×10^{-6}
Br ⁻ inflow concentration in the Zn experiment	c_{in}^{Br}	mmol/L	20.98	0.255
proportionality constant of sorbed concentrations for $\Delta\sigma''$	p	$\mu S\ g/(cm\ mmol)$	Na ⁺ : 259.25 Ca ²⁺ : -16.76 Zn ²⁺ : -7.22	Na ⁺ : 13.88 Ca ²⁺ : 1.38 Zn ²⁺ : 0.44
proportionality constant of Br ⁻ -concentrations for $\Delta\sigma''$	a	$\mu S\ L / (cm\ mmol)$	0.028	0.001

References

- Bromly M., Hinz C. and Aylmore L. A. G. (2007) Relation of dispersivity to properties of homogeneous saturated repacked soil columns. *European J Soil Science* **58**, 293–301.
- Strobel C., Abramov S., Huisman J. A., Cirpka O. A. and Møllgaard A. (2023) Spectral Induced Polarization (SIP) of Denitrification-Driven Microbial Activity in Column Experiments Packed With Calcareous Aquifer Sediments. *J. Geophys. Res. Biogeosci.* **128**.