

1 **Using complex resistivity imaging to infer biogeochemical processes associated**
2 **with bioremediation of a uranium-contaminated aquifer**

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Abstract

Experiments at the Department of Energy's Rifle Integrated Field Research Challenge (IFRC) site near Rifle, Colorado (USA) have demonstrated the ability to remove uranium from groundwater by stimulating the growth and activity of *Geobacter* species through acetate amendment. Prolonging the activity of these strains in order to optimize uranium bioremediation has prompted the development of minimally-invasive and spatially-extensive monitoring methods diagnostic of their in situ activity and the end products of their metabolism. Here we demonstrate the use of complex resistivity imaging for monitoring biogeochemical changes accompanying stimulation of indigenous aquifer microorganisms during and after a prolonged period (100+ days) of acetate injection. A thorough raw-data statistical analysis of discrepancies between normal and reciprocal measurements and incorporation of a new power-law phase-error model in the inversion were used to significantly improve the quality of the resistivity phase images over those obtained during previous monitoring experiments at the Rifle IFRC site. The imaging results reveal spatiotemporal changes in the phase response of aquifer sediments, which correlate with increases in Fe(II) and precipitation of metal sulfides (e.g., FeS) following the iterative stimulation of iron and sulfate reducing microorganism. Only modest changes in resistivity magnitude were observed over the monitoring period. The largest phase anomalies (>40 mrad) were observed hundreds of days after halting acetate injection, in conjunction with accumulation of Fe(II) in the presence of residual FeS minerals, reflecting preservation of geochemically reduced conditions in the aquifer – a prerequisite for ensuring the long-term stability of immobilized, redox-sensitive contaminants, such as uranium.

1. Introduction

A variety of industrial processes have left many sites around the world contaminated with radioactive wastes, such as uranium. Groundwater contamination is of particular concern because oxidized uranium is generally soluble in groundwater, and therefore mobile within the subsurface [Anderson *et al.*, 2003]. Thus, different techniques have been applied to effectively remove uranium from groundwater, such as pump and treat or permeable reactive barriers [e.g., Morrison *et al.*, 2006]. Unfortunately, such techniques have typically failed to ensure prolonged removal of uranium to levels mandated by regulatory agencies, thus leading to research into new remediation methods. Considering the redox behavior of uranium, bioremediation has emerged as an attractive alternative to lower the concentration of aqueous uranium in groundwater to acceptable levels. The governing idea is to promote the in situ immobilization of uranium through stimulation of indigenous microorganisms capable of reducing the soluble, oxidized form of uranium [U(VI)] to an insoluble form [U(IV)] [Lovley *et al.*, 1991; Gorby and Lovley, 1992]. Previous field studies have demonstrated the ability to remove aqueous uranium from groundwater by stimulating iron and sulfate reducing bacteria through injection of organic carbon [e.g., Anderson *et al.*, 2003; Vrionis *et al.*, 2005]. However, development of monitoring techniques with sufficient spatial and temporal resolution is still required to assess remediation efficacy at locations not directly sampled by groundwater monitoring wells and over long timescales.

Complex resistivity imaging has been demonstrated to provide valuable information for improved subsurface hydrological and environmental characterization [Kemna *et al.*, 2004; Hördt *et al.*, 2007]. This is due to the fact that the electrical induced polarization (IP), measured with the method in terms of resistivity phase, contains important

information about the geometry of the pore space, the characteristics of the mineral surface, and the ability to transfer electrical charge across the fluid-mineral interface [e.g., *Lesmes and Frye* 2001; *Binley et al.*, 2005]. Hence, complex resistivity imaging appears to be a suitable technique for monitoring changes in subsurface properties that accompany microbial activity, including the accumulation of reactive aqueous end products and the precipitation of metallic minerals.

As an example, consider the metabolic end products associated with the activity of iron and sulfate reducing microorganisms. Enzymatic reduction of ferric minerals by iron reducing bacteria (FeRB) leads to an increase in both aqueous and sorbed Fe(II), as well as changes in the mineralogy of the mineral phases (e.g., conversion of ferrihydrite to goethite and magnetite) [*Lovley et al.*, 2004]. The increase in aqueous sulfide ($\Sigma\text{H}_2\text{S}$) that accompanies the activity of sulfate reducing bacteria (SRB) leads to the precipitation of iron sulfides due to elevated concentrations of Fe(II) produced through both enzymatic and abiotic pathways (i.e., reduction of ferric minerals by $\Sigma\text{H}_2\text{S}$) [*Yao and Millero*, 1996]. Geophysical exploration of metallic ore deposits has deployed induced polarization and electrical resistivity methods for decades [e.g., *Marshall and Madden*, 1959; *Pelton and Smith*, 1976], with particularly strong IP responses reported for massive and disseminated metal sulfides [e.g., *Pelton et al.*, 1978; *Wong* 1979].

In recent years, laboratory measurements of the spectral induced polarization (SIP) response of biostimulated sediments have been used to delineate changes in physical and chemical properties following enhanced microbial activity [*Ntarlagiannis et al.*, 2005a; *Williams et al.*, 2005; *Personna et al.*, 2008]. At the field scale, anomalous IP signatures were found to correlate with the accumulation of iron sulfides following a

biostimulation experiment [Williams *et al.*, 2009]. While encouraging, these initial field results were based on data obtained at relatively sparse time intervals and with results reported for only two measurement frequencies (0.125 and 1 Hz). As such, better constrained SIP monitoring experiments are needed to (a) provide appropriate comparisons with laboratory SIP experiments and (b) quantify the effect of microbial activity on the measured signatures (i.e., computed images) at multiple stages during and after the remediation process.

In this study, we present time-lapse complex resistivity imaging results computed for data collected at regular intervals over a two-year period during and after acetate amendment. A thorough data analysis and an improved model to quantify the data error in the underlying inversion were applied to enhance the quality of the computed images. Based on our approach, we suggest that complex resistivity images can provide information – in quasi-real time – about aquifer redox status at different stages during the remediation processes. This is crucial to determine when further biostimulation (i.e., resumed injection of organic carbon) is required in order to maintain conditions favorable for the immobilization of redox sensitive contaminants, such as uranium. Although not directly studied here, the proposed complex resistivity monitoring approach is generally extendable to remediation approaches targeting contaminants other than uranium, such as metals and organic pollutants.

2. Material and Methods

2.1. Complex resistivity method

This section provides a short description of the complex resistivity method [for a more detailed review see, for example, Sumner, 1976; Telford *et al.*, 1990] and the

petrophysical controls on the measurements. The complex resistivity method is based on frequency-domain transfer impedance measurements, where each measurement involves four electrodes (two to inject current and two to measure the resultant voltage) and comprises magnitude (i.e., resistance) and phase (i.e., phase shift between current and voltage signals). Modern measuring devices can collect thousands of measurements in a few hours from electrodes located on the surface or in boreholes.

By means of an inversion algorithm [see, e.g., *Binley and Kemna, 2005*], a set of measured impedances can be converted into a distribution of complex resistivity values representing the subsurface. Multi-frequency or spectral IP involves impedance measurements over a wide range of frequencies (typically 0.01 to 1000 Hz) to gain information about the frequency dependence of complex resistivity. The complex resistivity ($\rho(\omega)$) can be expressed by its magnitude ($|\rho(\omega)|$) and phase ($\phi(\omega)$), by its real ($\rho'(\omega)$) and imaginary ($\rho''(\omega)$) components, and also in terms of complex conductivity ($\sigma(\omega)$):

$$\rho(\omega) = \rho'(\omega) + i \rho''(\omega) = |\rho(\omega)| e^{i \phi(\omega)} = 1/\sigma(\omega), \quad (1)$$

with $i^2 = -1$ and ω denoting the excitation frequency. The real part accounts for ohmic conduction (associated with energy loss), whereas the imaginary component is related to polarization (i.e., energy storage) as result of accumulation of charge and charge transfer reactions taking place along the fluid-mineral interface.

The magnitude of the complex resistivity (commonly simply referred to as resistivity) of sediments without electronically conductive minerals is mainly controlled by the

properties of the pore-filling electrolyte (i.e., electrical conductivity of the fluid), porosity, and by the connectivity of the pore space, with well-established petrophysical relationships enabling derivation of properties of interest (e.g., porosity and saturation) using resistivity data [Archie, 1942]. In contrast, the mechanisms underlying the resistivity phase response of sediments are less well understood and conclusive interpretation of IP data remains challenging, as does quantitative estimation of hydrologic and biogeochemical parameters derived from IP data-sets [e.g., Merriam, 2007; Slater, 2007; Williams *et al.*, 2009]. Nonetheless, recently developed mechanistic models describing the physicochemical properties of soils and sediments (in metal-free and bacteria-free porous media) that underlie the SIP response suggest an ever-improving ability to derive quantitative estimates from SIP data-sets [e.g., Leroy *et al.*, 2008; Revil and Florsch, 2010]. Additionally, stochastic estimation methods using SIP data and petrophysical relationships offer an approach for quantifying parameters of interest and their associated uncertainties, such as metal sulfide content and particle size distributions of pore clogging mineralization [Chen *et al.*, 2009].

Strong resistivity phase responses are related to the presence of metallic minerals in contact with an electrolyte [e.g., Marshall and Madden, 1959; Pelton *et al.*, 1978]. In the presence of metallic minerals (i.e., electronic conductors), the application of an external electrical field induces a change in the charge transfer mechanism from electrolytic (i.e., ionic transport in the pore fluid) to electronic (i.e., electron transfer within the metallic mineral) through electron transfer reactions at the fluid-mineral interface, associated with a phase shift between the applied current and the measured voltage. This mechanism is referred to as electrode polarization [for a complete description, see, e.g., Sumner, 1976; Angoran and Madden, 1977; Wong, 1979;

Merriam, 2007; *Revil and Cosenza*, 2010], and it is strongly related to the surface area and particle diameter of the (semi)conductive mineral grain [*Wong*, 1979; *Slater et al.*, 2005], as well as the electrolyte composition and aggregation state of the minerals [*Angoran and Madden*, 1977; *Williams et al.*, 2005; 2009].

Based on the strong phase response for metallic minerals, several studies have described the use of IP measurements for the detection and prospecting of buried ore mineralization, specifically metal sulfides [e.g., *van Voorhis et al.*, 1973; *Pelton and Smith*, 1976; *Wong*, 1979]. Further studies have demonstrated a proportional correlation between the size and volumetric enrichment of the metallic minerals and a characteristic frequency response (described by a characteristic relaxation time) [*Pelton et al.*, 1978; *Olhoeft*, 1985]. Recent laboratory studies have demonstrated a linear correlation between the imaginary component of the complex conductivity and the total metallic surface area of precipitated metallic minerals [*Slater et al.*, 2005; 2007], with other studies attributing changes in the frequency-dependent responses to variations in the concentration of electroactive ions in the pore fluid [*Angoran and Madden* 1979; *Wong*, 1979; *Williams et al.*, 2005] or spatiotemporal changes in location of the mineralization [*Ntarlagiannis et al.*, 2005a]. Given the multitude of condition-dependent factors controlling the complex resistivity response, further studies are warranted.

Lesser but measurable complex resistivity phase responses have also been reported for non-metallic minerals, related to polarization mechanisms in the electrical double layer surrounding mineral particles, denoted as electrochemical polarization [described in, e.g., *Lesmes and Morgan*, 2001; *Leroy et al.*, 2008]. Additionally, a membrane polarization mechanism [e.g., *Marshall and Madden*, 1959; *Titov et al.*, 2002] can also

exist when surface charge at the grain interface establishes a potential throughout the pore constituting ion-selective zones.

Additional factors may influence complex resistivity signatures associated with microbial activity. Formation of microbially-mediated minerals leads to an increase in total specific surface area, and, hence, enhancement of phase responses. The effect is enhanced if the precipitated minerals exhibit polarization properties (i.e. metallic minerals, such as FeS, which facilitate the change in charge transfer process) [Ntarlagiannis *et al.*, 2005a; Slater *et al.*, 2005; Williams *et al.*, 2005]. The stimulated growth of microbial cells is also related to an increase of surface area, suggesting a measurable increase of the phase response [e.g., Abdel Aal *et al.*, 2004; 2010; Davis *et al.*, 2006]; however, related studies have demonstrated that the polarization values generated at the microbial cell-fluid interface are significantly lower (<2 mrad) than the response generated by precipitated metallic minerals (~ 15 mrad) [Ntarlagiannis *et al.*, 2005b; Williams *et al.*, 2009]. Reversible reactions may also impact the complex resistivity signatures [e.g., Slater *et al.*, 2007], including changes in the geochemical composition of the groundwater and solid phase constituents. Particularly, the cessation of active biostimulation and organic carbon amendment delivery may lead to re-oxidation of reduced mineral phases (e.g., FeS) that in turn can generate a variety of (semi)conductive iron oxide minerals (e.g., ferrihydrite, lepidocrocite, goethite, etc.). Such a process can lead to additional changes in the surface area of pore-filling mineralization and further modify spatiotemporal complex resistivity signals.

2.2. Site description

The Rifle IFRC site is located near Rifle, Colorado (USA), on the grounds of a former uranium processing facility. An extended description of the site is given in many other works [e.g., *Anderson et al.*, 2003; *Vrionis et al.*, 2005; *Englert et al.*, 2009]. In general, an artificial clay-rich fill extends from the ground surface to a depth of ~1.75 m below ground surface (bgs). Beneath this fill are unconsolidated fluvial sediments composed of sand, silt, clay, and gravel. While varying seasonally by ca. 1 m, the average depth to groundwater in the vicinity of the complex resistivity study area is 3.5 m bgs and flow direction is toward the southwest. Reported iron bearing minerals in the unconfined aquifer consist of goethite, chlorite, magnetite, hematite, and pyrite [*Qafoku et al.*, 2009]. The low permeability Wasatch formation (composed of Eocene gravels, silts, and clays) underlies these sediments at a depth of ca. 6.5 m bgs and constitutes a lower boundary to groundwater flow.

2.3. Experimental set-up

As described by *Williams et al.* [2011], biostimulation via acetate injection was performed to reduce and immobilize U(VI) in the unconfined aquifer. Site groundwater was amended with bromide and acetate and introduced to the aquifer using ten injection boreholes (Figure 1). Fifteen monitoring wells were used to collect groundwater samples for geochemical analysis throughout the experiment, including three up-gradient and twelve down-gradient from the area of injection (Figure 1). The first experiment was initiated in August of 2007, during which acetate and bromide were injected over 31 days, with a target in situ aquifer concentration of 5 mM acetate and 2 mM bromide. An extended biostimulation experiment was performed in 2008. For the second experiment, the first 15-day injection period targeted an in situ acetate concentration of 5 mM, followed by 8 days where acetate-free groundwater was

injected. A second period of 5 mM acetate injection occurred over the next 15 days, followed by an increase to 15 mM on day 38 due to the complete consumption of acetate as a result of extensive sulfate reduction. Injection of elevated acetate (15 mM) continued through day 110, after which time injection ceased.

Complex resistivity measurements were collected periodically during both experiments (2007 and 2008) along two arrays (array A and B), which were oriented perpendicular to groundwater flow and were located approximately 3 and 6 m down-gradient from the injection gallery (Figure 1). Each array consisted of 30 electrodes with 1 m spacing for a total individual profile length of 29 m. The two arrays were parallel and centered with respect to the injection gallery (Figure 1). For the 2007 experiment, measurements were obtained before injection began and then every 12 days during the injection interval; a final data-set was collected 8 weeks after the injection ceased. For the 2008 experiment, the measurements were collected every 3 days during the injection cycle and every 2 and 6 months afterwards over the course of a year. Measurements in 2007 were collected at 1 and 4 Hz, similar to *Williams et al.* [2009]; while the data collected in 2008 were acquired over the 0.25 to 64 Hz frequency range, attempting to record a wider spectral response. A summary of the different acetate injections, their duration and details on the acquisition of complex resistivity measurements is presented in Table 1.

Non-polarizing metal-metal salt (Cu/CuSO_4) electrodes were deployed in order to minimize unwanted effects due to polarization of the electrodes, which are particularly critical for measurements made at low frequency (<10 Hz), as noted in previous studies [e.g., *LaBrecque and Daily*, 2008]. The measurements in this study were carried out

using a dipole-dipole configuration with a skip-3 protocol (i.e., each dipole skipping 3 electrodes, resulting in a dipole length of 4 m for the current and potential dipoles). This measurement protocol has been used in a previous study [Williams *et al.*, 2009] showing a good resolution for depths up to 7 m, and reasonable acquisition times. The selection of an appropriate measuring protocol plays a significant role regarding the resolution of the images and it has been the issue of several works [e.g., Bing and Greenhalgh, 2000; Stummer *et al.*, 2004]. It is also important to remark that measurements of complex resistivity performed at low frequencies (< 1 Hz) require large acquisition times (up to several hours). Regarding all this, the aim is to find the best compromise between high signal-to-noise ratio (favored by large dipole lengths), high resolution (favored by small dipole lengths) and short acquisition times (determined by the number of independent measurements). At the same time it is also important to avoid measurements where the potential electrodes are placed inside the current dipole and those with a large separation between dipoles (restricting the depth of penetration of our measurements) in order to reduce inductive coupling [e.g., Pelton *et al.*, 19878].

2.4. Inversion approach

Our investigation is based on complex resistivity images obtained using the smoothness-constraint inversion code by Kemna [2000]. The algorithm calculates the complex resistivity distribution on a 2D grid of lumped finite-element cells from a given data-set of transfer impedances (Z_i , $i = 1, \dots, N$; with N being the number of measurements), at a given frequency. Within the inversion, log-transformed impedances are used as data and log-transformed complex resistivities as parameters. Through using log-transformed values, it is possible to account for the typical large range in the

resistance values of data-sets and of electrical resistivity values in the subsurface, respectively. The inversion algorithm iteratively minimizes an objective function, $\Psi(\mathbf{m})$, which is composed of the measures of data misfit and model roughness, with both terms being balanced by a real-valued regularization parameter, λ :

$$\Psi(\mathbf{m}) = \left\| \mathbf{W}_d [\mathbf{d} - \mathbf{f}(\mathbf{m})] \right\|^2 + \lambda \left\| \mathbf{W}_m \mathbf{m} \right\|^2, \quad (2)$$

In equation (2), $\mathbf{d}$ is the complex-valued data vector ($d_i = \ln Z_i$), $\mathbf{m}$ is the complex-valued model vector ($m_j = \ln \rho_j; j = 1 \dots M$; with M being the number of parameter cells), $\mathbf{f}(\mathbf{m})$ is the complex-valued operator of the forward model, $\mathbf{W}_m$ is a real-valued matrix evaluating the first-order roughness of $\mathbf{m}$, and $\mathbf{W}_d$ is a complex-valued data weighting matrix. Assuming uncorrelated and normally distributed data errors, $\mathbf{W}_d$ is diagonal and given by

$$\mathbf{W}_d = \text{diag} \left\{ \frac{1}{\varepsilon_1}, \dots, \frac{1}{\varepsilon_N} \right\}, \quad (3)$$

with

$$\varepsilon_i = s(\ln |Z_i|) + i s(\varphi_i), \quad (4)$$

where $s(\ln |Z_i|)$ and $s(\varphi_i)$ represent the real-valued data error (standard deviation) of the log magnitude (i.e., resistance), $|Z_i|$, and the phase, φ_i , respectively, of the impedance $Z_i = |Z_i| e^{i\varphi_i}$. Note that $d_i = \ln |Z_i| + i \varphi_i$, and that Equation 4 describes an error ellipse in

the complex plane around d_i . The iteration process is stopped when the RMS data misfit,

$$RMS = \sqrt{\frac{1}{N} \sum_{i=1}^N \frac{|d_i - f_i(\mathbf{m})|^2}{|\varepsilon_i|^2}}, \quad (5)$$

reaches a value of one for a maximum possible value of λ , yielding the smoothest model subject to fitting the complex data within the error ellipse defined by ε_i .

Once the complex data misfit has reached an RMS value of one, it is possible to run additional inversion iterations purely for the phase (i.e., keeping the already inverted magnitude image fixed) in order to improve the phase image. This is critical, given that the log resistance error is typically one order of magnitude larger than the phase error [Kemna, 2000]. Kemna [2000] refers to this step as “final phase improvement”, because it yields an image with “improved” quality for the phase. Note that in the final-phase-improvement step the same inversion framework is used as outlined above, but with all data and model quantities referring only to the phase. More details on the inversion scheme and the underlying modeling algorithm are given in Kemna [2000].

2.5. Data error parameterization

The quantification of the data error plays a significant role in the quality of the final images and thus in their interpretation. Images with low contrast (i.e., resolution) may result from an overestimation of the data error (i.e., under-fitting in the inversion), whereas under-estimating the data error leads to over-fitting in the inversion and artifacts in the images [e.g., LaBrecque *et. al.*, 1996].

Although it is impossible to know the exact variance and distribution of the error in the data, approaches have been developed to provide estimates. For tomographic data-sets, analysis of the misfit between normal and reciprocal measurements has commonly been used to estimate the error present in the data [e.g., *LaBrecque et al.*, 1996; *Slater and Binley*, 2006]. In order to perform reciprocal measurements, it is necessary to reacquire the data for each quadrupole after interchanging the current and potential electrodes. This procedure permits one to account for random errors in the data associated with fluctuations in injected current, changes in the contact resistance between the electrodes and the ground surface, and other unsystematic errors [*Binley et al.*, 1995]. Systematic errors are those which show a correlation within the data-set (e.g., malfunction of a particular electrode or measuring channel, or poor galvanic contact). Systematic errors should be corrected, if possible, or deleted from the data-set prior to the inversion. Particular sources of systematic errors for IP measurements include polarization of the electrodes [e.g., *Dahlin et al.*, 2002] and electromagnetic coupling [e.g., *Pelton et al.*, 1978].

In this study we estimate the error for resistance measurements based on the model proposed by *LaBrecque et al.* [1996], which has been used in various studies [e.g., *Kemna et al.*, 2002; *Köstel et al.*, 2008; *Oberdörster et al.*, 2010]. This model is based on a linear relationship between the measured resistance, R ($R = |Z|$), and its error, $s(R)$, written as

$$s(R) = a + bR , \tag{6}$$

with appropriately chosen parameters $a, b > 0$.

For impedance phase (φ) measurements, the assumption of a constant error value has been commonly used [e.g., *Kemna et al.*, 2004; *Williams et al.*, 2009]. In this study, we applied a recently developed error model to quantify the phase error, $s(\varphi)$, as a power-law function of resistance, that is governed by the voltage signal strength for constant currents, written as

$$s(\varphi) = aR^b, \quad (7)$$

with appropriately chosen parameters $a > 0$ and $b < 0$ (different from those in Equation 6). Usage of the power-law error model (Equation 7) in the inversion provides images with fewer artifacts and larger contrast relative to those computed using previous approaches (Flores Orozco et al., *submitted to Geophysics*, 2010).

Measurements of contact resistances were performed before each data acquisition with observed values in the order of $\sim 500 \, \Omega$; the current injection was performed with a constant voltage of 55 V, resulting in injected currents of 100-200 mA. Outliers were defined as (a) those measurements performed with injected currents below 10 mA, and (b) measurements with a difference between normal and reciprocal values exceeding two times the standard deviation (of the normal-reciprocal misfit) of the entire data-set. After removal of outliers, average values of normal and reciprocal measurements were used for the inversion, consisting of approximately 390 data points per data-set. Error parameters (a and b in Equations 6 and 7) were quantified by means of statistical analyses in a set of resistance ranges as described in Flores Orozco et al. (*submitted to*

Geophysics). Independent error parameters were computed for each data-set collected at different times and frequencies.

3. Results

The images of resistivity magnitude ($|\rho|$) and phase (ϕ) (subsequently referred as resistivity and phase, respectively, for the sake of simplicity) computed for baseline data collected along arrays A and B are presented in Figure 2. For the resistivity images, the inversion algorithm solves for the same model for both frequencies deployed; for conciseness we present only the image computed for the data collected at 1 Hz. The structures visible in the images of arrays A and B are consistent with the stratigraphy of the site (as presented in the lithologic column in Figure 2 for comparison), which consists of three principal units. The thin, shallowest layer, which is characterized by low resistivity values ($\sim 10 \Omega\text{m}$), corresponds to the clay-rich fill material that covers most of the Rifle IFRC site. The middle unit is comprised of fluvial sediments and is characterized by more resistive sand, silts, and gravels (values between $100\text{--}400 \Omega\text{m}$), with a thickness of $\sim 4.5 \text{ m}$. Lateral variations observed in this resistive unit are interpreted to be due to heterogeneities in the alluvial sediments of the aquifer, as evidenced by a wide range of grain sizes ($<1 \text{ mm}$ to $>10 \text{ cm}$) recovered during drilling. The relatively low resistivity values ($\sim 100 \Omega\text{m}$) observed near the center of the images (between 10 and 20 m along the direction of the array) correlate with the presence of more clay-rich sediments, as documented during geological logging of the recovered sediments. The lower unit corresponds to the silt-rich and less resistive Wasatch formation ($<70 \Omega\text{m}$).

For array A, the presence of heterogeneities near the center of the array is also noticeable in the phase images (Figure 2). The phase response at both frequencies (1 Hz and 4 Hz) reveals a significant polarizable anomaly extending between 3 and 7 m bgs in the center of the images (between 10 and 20 m in the direction of the array). The 4 Hz phase image reveals a more polarizable anomaly (~ -18 mrad) than the 1 Hz image (~ -12 mrad). For array B, the images show a similar resistivity structure but significantly lower absolute phase values (~ 5 mrad) relative to the array A images.

The consistency between the phase values observed along array A and those reported for previous complex resistivity measurements at the Rifle site collected elsewhere during acetate based biostimulation experiments [Williams *et al.*, 2009] suggests the accumulation of reduced biogeochemical end products, such as Fe(II), FeS, and FeS₂ in the region of strong phase response on array A. Indeed, analysis of recovered material from several holes drilled in the vicinity of the anomaly of array A documented sediments enriched in refractory organic carbon, total reduced inorganic sulfur (e.g., FeS, H₂S, and S⁰), framboidal pyrites, and uranium [Qafoku *et al.*, 2009]. Recovered sediments during the drilling of observation wells along array B (D-09, D-10, D-11, D-12) contained visibly more oxidized sediments, with a far lower abundance of metal sulfides and sorbed Fe(II), as compared to sediments in the vicinity of array A. Such results may help explain the variation in the baseline phase response observed along arrays A and B. Referred to as zones of natural bioreduction, these regions are characterized by trapped organic matter that sustains slow but elevated rates of microbial activity that in effect replicate the same suite of biogeochemical reactions that accompany acetate amendment (albeit over much longer timescales). Such reactions

include the accumulation of Fe(II) and insoluble sulfide minerals that track slow rates of iron and sulfate reduction, respectively.

The monitoring results presented in this study pertain primarily to data collected along array A, which exhibited a stronger phase response over the 2007 and 2008 injection cycles relative to array B. While possibly a consequence of subsurface heterogeneity described above, the larger temporal phase response observed along array A is likely related to elevated rates of microbial activity and more extensive mineral precipitation occurring in closer proximity to the injection gallery. Although larger in magnitude, variations in the phase response observed along array A were largely consistent with those observed along array B.

The resistivity and phase images computed for data collected along array A during and after acetate injection in 2007 are presented in Figure 3. While negligible change in resistivity was observed over the injection interval, the phase response at two frequencies (1 and 4 Hz) decreased following the short-duration acetate injection. The last time point for which data was collected (88 days after the injection was stopped) reveals the virtual disappearance of the baseline phase anomaly, with the images revealing low overall absolute phase values (<5 mrad) across the zone of injection.

The second biostimulation experiment began in July 2008, 361 days after the first injection. The resistance values measured exhibited negligible variations throughout the 2008 experiments (for the different frequencies collected), with values consistent with those observed in 2007. In contrast, significant variability in the phase response at different measurement times was observed, particularly for the lowest frequency

collected (0.25 Hz), as presented in the histograms of the resistance and phase measured values for selected days post initial 2007 acetate injection (Figure 4).

The phase images associated with the second biostimulation experiment are shown in Figure 5. Here the images at frequencies below 1 Hz show the strongest phase anomalies during the injection period (days 361 to 426), with absolute values above 10 mrad; these values decrease significantly for the images between days 393 and 396. For the images after day 450 – shortly after finishing the last injection – the values begin to increase rapidly. The largest phase anomalies exceeded 40 mrad (in absolute values) and persisted for hundreds of days after acetate injection ceased and long after both acetate and bromide were lost from the system.

For data collected at higher frequencies (>1 Hz), sediments exhibited a less anomalous phase response with time over the injection interval, with anomalies between -6 and -10 mrad. The images show a consistent result as a function of time, with absolute phase values generally decreasing as frequency increases. Similar to the low-frequency data, the strongest phase anomalies were observed after injection ended (day 461), with maximum absolute values 20-30 mrad greater than their pre-injection value. Data collected at higher frequencies are not presented, as analysis of the raw data showed poor data reciprocity and evidence of significant electromagnetic coupling.

To better illustrate the advantages of the phase data error parameterization deployed (Equation 7), we also present the images obtained using the assumption of a constant phase error value (Figure 6a), as used by *Williams et al.* [2009]. For brevity, we only present the images computed for representative times and for data collected at 0.25 Hz,

where more pronounced temporal phase changes were observed. The constant phase data error for each data-set was computed based on the analysis described by *Slater and Binley* [2006]. The images obtained with a constant phase error show similar structures to those obtained with the power-law error model for the corresponding days (Figure 5), but they are more impacted by inversion artifacts (particularly for measurements collected before or after acetate injection at frequencies below 4 Hz) or of poor contrast (i.e., poor resolution exhibited in images for data collected during the periods of acetate injection, especially at 4 Hz).

The inversion of tomographic complex resistivity data-sets collected at different frequencies (or time-lapses) has not received enough attention to date; it has been a subject of only a few studies [e.g., *Kemna et al.*, 2000; *Hördt et al.*, 2007; *Commer et al.*, 2011]. A recent study demonstrated the advantages of defining individual error parameters (i.e., for each frequency) for tomographic SIP data collected over a wide frequency band (*Flores Orozco et al.*, *submitted to Geophysics*, 2010). For the data collected in the present study, the inversion performed with individual error parameters (computed for each frequency and time-lapse) solved for images exhibiting features consistent for similar conditions at different periods during the experiment (i.e., a consistent phase response was observed in the images for data collected in the course of each amendment injection).

An alternative procedure is to invert all data-sets assuming the same error level (i.e., with identical error parameters). The aim is to avoid the comparison of images with a different level of fitting (i.e., smoothness). Inversion results computed using the highest error parameters found (for each frequency) by means of the power-law error

parameterization are presented in Figure 6b. These images show similar structures as the images computed by means of individual error model parameters (Figure 5), albeit with slightly lower contrast, as expected, due to over-estimation of the error. For completeness, we present in Figure 6c the images obtained using a constant phase error defined by the highest value found, which leads to significantly decreased contrast in the images compared to Figure 6a.

Other approaches may include merging all data collected (for single or multi-frequencies) and computing the error parameters characterizing the composite data-set; or using the average value of the computed error model parameters of the individual data-sets (for data collected at different times and/or frequencies). Both approaches were tested here resulting in images strongly affected by artifacts (data not shown). The definition of common error parameters applicable to data-sets collected at single or multiple frequencies is challenging, if not impossible, and such a solution may ultimately require a trial and error approach, not suitable for the monitoring purposes of this study. As a result, our interpretation and discussion refers solely to those images obtained by means of individual error parameters, as presented in Figures 2, 3, and 5.

To better highlight the phase response for different times, we plotted it against the elapsed time for the two years of monitoring, starting with the baseline measurements collected before the first acetate injection in 2007 (Figure 7). The phase value plotted represents a pixel in the vicinity of the observation well D-01, defined by the value of the model parameters between 4.5 and 5.5 m bgs and 18 and 20 m along the direction of the profile. For comparison, we present in Figure 7 the plots of relevant geochemical parameters observed in groundwater samples collected in well D-01.

The observed geochemical and geophysical responses (Figure 7) are consistent for all the experiments (i.e., injections) performed in 2007 and 2008, with slight variations between them due to the different concentrations of injected acetate. Considering the response observed in the Figure 7, four different periods can be easily distinguished:

3.1 Period dominated by iron reduction

For all acetate injections performed, a rapid decrease in the concentration of dissolved uranium is observed coincident with a significant decrease in the absolute phase values. As noted, the injection of acetate stimulates the growth of *Geobacter* strains capable of reducing U(VI) to insoluble U(IV) [Anderson *et al.*, 2003; Vrionis *et al.*, 2005; Li *et al.*, 2009]. Members of the *Geobacteraceae* grow primarily by enzymatically reducing Fe(III) oxides present in aquifer sediments [Finneran *et al.*, 2002; N'Guessan *et al.*, 2008], resulting in the accumulation of Fe(II) in the vicinity of the mineral grain [Williams *et al.*, 2009]:



The increase in Fe(II) just after the amendment injection (e.g., at day 35 and 360 in Figure 7) is concurrent with rapid removal of U(VI). Phase images at this time reveal a slight decrease, most probably as a consequence of an increase in the electrical conductivity due to the injection of acetate and bromide.

3.2 Periods dominated by sulfate reduction

After day 55, a rapid decrease in dissolved Fe(II) was observed, coinciding with increasing aqueous sulfide ($\sum\text{H}_2\text{S}$) accompanying the activity of SRB. As the amount or reactivity of available Fe(III) shrinks following prolonged acetate injection, SRB are more readily able to compete for acetate (electron donor):



The shift to a period dominated by sulfate-reducing conditions can be characterized by less effective removal of U(VI) if acetate levels are lowered to levels insufficient to support continued activity of *Geobacter* strains capable of U(VI)-reduction [Williams *et al.*, 2011].

3.3 Precipitation of iron sulfides

During the 2007 experiment, a very short-lived period of sulfate-reduction was observed at later times (day 70). For the 2008 injections, large concentrations of $\sum\text{H}_2\text{S}$ were observed, which resulted in complete titration of aqueous Fe(II), mainly between days 390 and 490, presumably as iron monosulfides (FeS):



This period of rapid Fe(II) consumption is characterized by low, but non-zero, absolute phase values (<10 mrad) over all frequencies. The precipitation of new metallic minerals (FeS) within the pore space constitutes an increase in surface area (where induced polarization takes place), thus an increase in the phase response may be expected, as reported for laboratory measurements [e.g., Slater *et al.*, 2005]. However,

our results reveal a significant decrease in the absolute phase values. We suggest that this decrease could be related to the depletion of electroactive ions (primarily dissolved Fe(II)), the absence of which manifests itself as a lower overall phase response, as suggested by *Williams et al.* [2009]. The importance of electroactive ions in controlling the polarization magnitude at the metallic interface has been extensively discussed in previous studies [*Angoran and Madden*, 1977; *Wong*, 1979; *Merriam*, 2007].

3.4 Post injection

Measurements collected approximately one month after the injection was finished (> 490 days) show a significant increase in the absolute phase values, for all frequencies, with the highest values reported at the lowest frequency (> 40 mrad for data collected at 0.25 Hz). We interpret this large phase response to be a result of further accumulation of metallic sulfides and electroactive ions Fe(II). The high phase values were also observed for measurements collected one year later (day 705) for similar concentrations of dissolved Fe(II) and (presumably) similar enrichments of metallic sulfides (FeS), suggesting that co-occurrence of FeS and Fe(II) engenders the most significant phases anomalies – even in the absence of sustained organic carbon amendment. Such results strongly suggest the value of the complex resistivity monitoring method for tracking the long-term evolution of aquifer redox status following cessation of active biostimulation.

4. Discussion

The very different geochemical conditions that accompanied the short- (2007) and long-duration (2008) injection periods yielded characteristic complex resistivity signatures. The low overall concentration of $\Sigma\text{H}_2\text{S}$ and minimal decrease in Fe(II) during the 2007 experiment suggest negligible precipitation of metal sulfides, which correlates to

minimal changes observed in the phase response. On the opposite, the high concentration of dissolved Fe(II) and $\sum\text{H}_2\text{S}$ followed by an abrupt decrease of both, e.g., at day 390, suggest the formation of new biominerals (FeS) during the 2008 experiment. While fluctuations in the phase response were observed during the injection period, the large increases in the phase response above pre-injection levels indicate the method's sensitivity to both mineral precipitation reactions and the resultant pore fluid chemistry.

A strong increase in the phase response would be expected accompanying the precipitation of iron sulfides, which are characterized by high surface area and semi-conductive properties. However, the images computed indicate only moderate phase values (absolute values <10 mrad) during the time period when geochemical data suggests that precipitates should be formed, given by low concentrations of Fe(II) and decrease in the concentrations of S(2-). This can be explained by the low concentration of electroactive ions, specifically aqueous and/or sorbed Fe(II). To better highlight this, we present in Figure 8 plots of the geoelectrical response against the concentration of the most significant geochemical parameters (i.e., Fe(II) and $\sum\text{H}_2\text{S}$). Geochemical concentrations were measured in water samples collected in the observation wells along array A (i.e., D-01 to D-04); while the geoelectrical data represent the mean value of a pixel corresponding to the model parameters between 4.5 and 5.5 m bgs and with a width of 1 m (centered at the position of the corresponding observation wells). In the plots of Figure 8, it is possible again to see that there is no clear correlation between σ' and changes in the geochemistry of the groundwater. On the opposite, plots of the phase response (for all frequencies studied) show a strong correlation ($R^2 > 0.94$) where the phase values increase proportionally to the concentration of Fe(II), for concentrations of

Fe(II) above a threshold value (50 μM). In order to dismiss the effect of changes in the electrical resistivity of the fluid, due to the injections of acetate and bromide, it is important also to look at the imaginary component of the complex conductivity (σ''). Regarding this, plots of Figure 8 exhibit also a strong correlation ($R^2 > 0.95$) between σ'' and concentrations of Fe(II), again for Fe(II) concentrations above a threshold value of 50 μM . For the plots corresponding to the concentrations of $\Sigma\text{H}_2\text{S}$, it is easy to distinguish a significant decrease in the value of σ'' and phase for concentration of $\Sigma\text{H}_2\text{S}$ exceeding 3 μM , independent of the frequency used to perform the measurements. For completeness, the plot of the concentrations of $\Sigma\text{H}_2\text{S}$ and Fe(II) is provided in Figure 9. As expected, a strong ($R^2 > 0.97$) negative correlation is observed between them, validating the sensitivity of the complex resistivity method to distinguish changes related to variations of the chemical composition of the fluid. The consistent response of the phase and σ'' demonstrates that variations in the subsurface delineated in the phase images are correlated with the induced microbial activities and not with changes in the groundwater conductivity due to the amendment injection.

Besides the variations in fluid chemistry, the significant decrease in the phase and σ'' values observed for measurements collected during acetate injection might also be a consequence of the extremely small size of the iron sulfides, most probably resulting in a critical frequency (i.e., the frequency at which the maximum phase response is observed) significantly higher than collected in this study. Results from zero-field Mossbauer spectroscopy performed on similar Rifle reduced sediments show abundant iron sulfides in the $<53\ \mu\text{m}$ fraction [Qafoku *et al.*, 2009], and freshly precipitated FeS phases during acetate amendment are expected to be very finely particulate, with particle sizes of tens to hundreds of nanometers [Williams *et al.*, 2005]. As such, wider

frequency-band complex resistivity data are likely necessary to capture a significant response for very fast reactions at the interface between the groundwater and the formed iron sulfide mineral. However, in practice, it is necessary to overcome the problem of unwanted inductive and capacitive coupling noise that commonly corrupts higher frequency complex resistivity field data-sets, which is a current topic of research [e.g., Zimmermann *et al.*, 2008].

In addition, recent studies in column experiments have demonstrated the concurrent precipitation of calcite during acetate injection at Rifle, with the effect being most pronounced during sulfate reduction [Li *et al.*, 2009]. Measurements of electrical properties have demonstrated that calcite can act as an insulator for the frequency range studied here [Wu *et al.*, 2009; 2010], suggesting that the low absolute phase values observed in 2008 (days 400-450) may be associated with calcite minerals impeding the contact between the metallic minerals and the electrolyte. Subsequent precipitation of FeS and the accumulation of Fe(II) after the injection is stopped might overcome the insulating effect of calcite precipitation (especially if it is heterogeneously dispersed across mineral surfaces), corresponding to increase in the phase and σ'' values.

Figure 10 presents a modification of Figure 7, in order to present the variations of the real (σ') and imaginary (σ'') components of the electrical conductivity for the selected pixel over the two year monitoring period. Looking at variations in the real and imaginary components is particularly useful to distinguish effects related to the growth of biofilms or nanowires as reported in other works [e.g., Atekwana and Slater, 2009, and references therein].

Plots of the real component reveal a significant increase over measurements performed in 2007 compared to those performed in 2008-2009. This is possibly related to mineralogical changes following the 2007 injection, but more likely attributable to the increase in fluid conductivity after the first injection in 2008 due to the higher concentration of acetate injected. It is also important to note that the imaginary component exhibited negligible increase during the 2007 injection experiment. Microbial activity and, hence, growth and cell synthesis was unambiguously stimulated during the 2007 experiment, as predicted [Li *et al.*, 2009] and evidenced by a wide range of biogeochemical data [Mouser *et al.*, 2009; N'Guessan *et al.*, 2009; Elifantz *et al.*, 2010; Williams *et al.*, 2011]. Furthermore, analysis of groundwater proteomic samples obtained from wells D-05 and D-07 during the 2007 biostimulation experiment demonstrated a shift in *Geobacter* growth habit from planktonic to attached [Wilkins *et al.*, 2009], indicative of biofilm formation. Laboratory experiments have suggested that an accumulation of cell surfaces following stimulation and growth, as well as the formation of biofilms, can increase in the imaginary component of the complex conductivity of sediments [Ntarlagiannis *et al.*, 2005b; Davis *et al.*, 2006; Abdel Aal *et al.*, 2004; 2010]. However, our 2007 complex resistivity monitoring experiments suggest that extension of such laboratory results to the field may be challenging. While the accumulation of cell surfaces and the formation of biofilm structures may impart modest increases in the imaginary component of the complex conductivity signature of subsurface sediments, our results indicate that such effects may be too low to be detected at field-relevant scales (e.g., depths greater than a few meters). In contrast, variations in electroactive fluid composition and precipitation of semi-conductive minerals of varying surface area can induce large polarization effects that significantly

deviate from pre-stimulation values, with such effects readily detectable at field-relevant scales.

5. Conclusions

We collected and inverted an extensive time-lapse complex resistivity data-set associated with a bioremediation experiment and interpreted the resulting images through joint consideration of geochemical and microbiological measurements. We illustrated the sensitivity of the inverted images to an appropriate error description and highlighted the impact that varied error descriptions can have on the interpretation of complex resistivity images in terms of biogeochemical processes. The extended data analysis and error description significantly improved the quality of the images over those obtained during previous complex resistivity monitoring experiments at the IRFC Rifle site [Williams *et al.*, 2009].

The improved imaging procedure and extensive long-term data-set facilitated interpretation of the complex resistivity images to a range of biogeochemical initial conditions and remediation-induced processes. For this experiment, the resistivity images alone failed to provide meaningful information about bioremediation-induced processes; the inversion results provided information about baseline heterogeneity but indicated little response over time to the biostimulation. In contrast, the phase images exhibited strong sensitivity to variations in fluid chemistry and the precipitation of semi-conductive minerals, with an important decrease in the response for low frequencies (0.25 Hz) when dissolved iron was depleted from the groundwater, whereas higher frequencies (4 Hz) revealed a detectable increase in the phase response. Post-injection data exhibited very high absolute phase values, suggesting that the iterative

precipitation of polarizable minerals (FeS) and accumulation of electroactive species, such as Fe(II), are capable of generating the most pronounced phase anomalies.

Based on our results, and consistent with previous studies [Williams *et al.*, 2005; 2009], we can conclude that electrode polarization (when both metallic minerals and electroactive ions are present) is the principal polarization mechanisms underlying the response observed. A strong correlation is observed between high concentrations of Fe(II) and the imaginary component of the complex conductivity, as well as for the phase, for periods when concentrations of Fe(II) were above a threshold value of ca. 50 μM . For periods dominated by sulfate-reduction, when the concentration of electroactive compounds (e.g., Fe(II) and perhaps other redox-sensitive metals) is below a critical concentration (50 μM for our study), electrode polarization is minimized and other polarization mechanisms, such as electrochemical or membrane polarization, dominate. Such periods are characterized by a moderate phase response (absolute phase values below 10 mrad) in spite of the existence of metallic and clay minerals. A schematic representation summarizing the different conditions enhancing the observed phase response is presented in the Figure 11.

Complex resistivity monitoring of the studied bioremediation experiments provided a characteristic response for four different processes: (i) delineation of natural bioreduction zones, where uranium is slowly removed from groundwater without amendment injections, characterized by a strong phase response, particularly at the highest measuring frequency; (ii) a noticeable decrease in the phase response (for all studied frequencies) was observed for measurements just after acetate injection during periods dominated by iron-reduction, characteristic of fast rates of uranium removal;

(iii) low absolute phase values were observed for periods dominated by sulfate-reduction, characterized by less effective uranium removal; (iv) a significant increase in the phase response was observed for measurements collected after cessation of the amendment injection, consistent with subsequent decrease in dissolved U(VI). The described phase response is also observed for the imaginary component of complex conductivity (σ''), indicating that the processes delineated are not controlled by variations in the fluid conductivity associated with the amendment injection. As such, complex resistivity imaging might be a useful tool to determine when further biostimulation (i.e., resumed injection of organic carbon) is required in order to maintain conditions favorable for the immobilization of redox sensitive contaminants, such as uranium.

More research is warranted to better understand the observed phase response and the sensitivity of the frequency-dependent response to specific biogeochemical changes (e.g., ion accumulation and depletion, mineral precipitation, etc.). Although microbial activity appears capable of generating large field-scale phase anomalies – with changes in fluid chemistry likely dominating the response – the mechanisms underlying the phase response are still open to debate. Data collection over a wider frequency band is critical for a more accurate understanding of the microbial and chemical processes ongoing during acetate amendment. Inversion of the complex resistivity measurements based on a time- or frequency-regularization scheme might be helpful to increase the resolution and reliability of the final images.

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8. Figure captions

Figure 1: Schematic representation of the experimental set-up. Monitoring wells up-gradient (o) and down-gradient (●) of the injection gallery (solid black rectangle) are referred to the direction of the groundwater flow (solid arrow). The dashed lines represent the location and extent of the array A and B. All the dimensions are given in meters.

Figure 2: Complex resistivity images of the baseline data collected for array A and array B. Left: resistivity images for data collected at 1 Hz. Middle and right: phase images computed for data collected at 1 and 4 Hz, respectively. The depth of the water table is marked for each image (solid line), as well as the position of the electrodes at the surface (black points). Black lines in the top images indicate the location of observation wells D-04, D-03, D-02, and D-01 for Array A; and D-12, D-11, D-10 and D-09 for Array B (from left to right). On the bottom a representative lithologic column of the site is given for comparison.

Figure 3: Complex resistivity images for the measurements collected along array A in 2007 after an injection of 5 mM acetate and 2 mM bromide. Elapsed time in days is referenced to the start of acetate injection. Left: resistivity images for data collected at 1 Hz. Middle and right: phase images computed for data collected at 1 and 4 Hz, respectively.

Figure 4: Histogram of measured resistances and phase values along array A at 0.25 Hz. Elapsed time in days is referenced to the start of acetate injection in 2007.

Figure 5: Selected phase images for the data collected at different times and frequencies along array A during 2008-2009. Elapsed time in days is referenced to the start of acetate injection in 2007.

Figure 6: Selected phase images inverted by means of different error parameterizations: a) individual error parameters considering a constant phase data error value; b) highest error parameters considering a power-law error model (Equation 7); and c) highest value considering a constant error value. Data were collected at 0.25 Hz along array A during 2008-2009. Elapsed time in days is referenced to the start of acetate injection in 2007.

Figure 7: Detected concentrations in observation well D-01 of dissolved uranium (U[VI]) (in the first column), acetate (Ac-) and bromide (Br-) (second column), and dissolved Fe(II), S(2-) and Na+ (third column). For comparison the phase values of a selected pixel (in the vicinity of the well D-01) extracted from the inverted images for data collected at different frequencies (fourth column). Elapsed time in days is referenced to the start of acetate injection in 2007.

Figure 8: Correlation plots between the geoelectrical response and relevant geochemical parameters. Measured concentrations of Fe(II) and S(2-) in the observation wells (D-01, D-03 and D-04) are plotted against the complex conductivity values (real and imaginary components in the first and second plot, respectively, and the phase in the third column). Values of complex conductivity are given by the mean value of a pixel covering the model parameters from 3.5 to 6 m bgs and with an extension of 1 m centered at the position of the corresponding observation wells.

Figure 9: Correlation plot of the measured concentration of dissolved Fe(II) and S(2-) in the observation wells along Array A.

Figure 10: Plots of the real (σ' , at the top) and imaginary (σ'' , at the bottom) components of the complex conductivity. Values are given for a selected pixel close to the observation well D-01. Elapsed time in days is referenced to the start of acetate injection in 2007.

Figure 11: Schematic representation of the polarization mechanisms underlying the observed phase response during the two years of bioremediation monitoring. The solid black structures (e.g., FeS) represent metallic minerals, the gray bodies represent other kind of polarizable minerals (e.g., calcites, clays) and the solid circles represent electroactive ions (e.g., FeII) present in groundwater. Here 3 possible scenarios are considered: (a) Electrode polarization as the dominating polarization process, taking place on the surface of precipitated metallic minerals, characterized by high polarization (σ'' and phase) values if a critical concentration (represented by the dashed line) of electro-active ions ($\text{Fe(II)} > 50 \mu\text{M}$ for our experiments) is present in the groundwater. Membrane polarization will be the dominating polarization processes, related to modest σ'' and phase values, for the cases that: (b) metallic minerals have been precipitated but concentration of electroactive ions are lower than the critical concentration (i.e., periods of dominating sulfate reduction in our experiments); and (c) for a negligible amount of metallic minerals.

Table 1: Timeline of the different amendment injections and details on the acquisition of complex resistivity measurements.

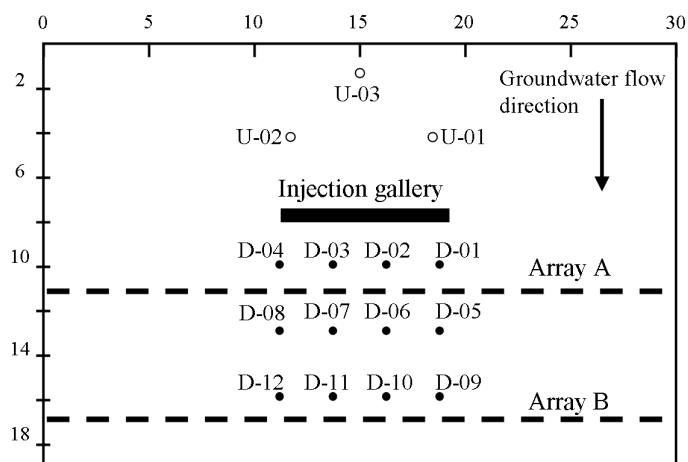


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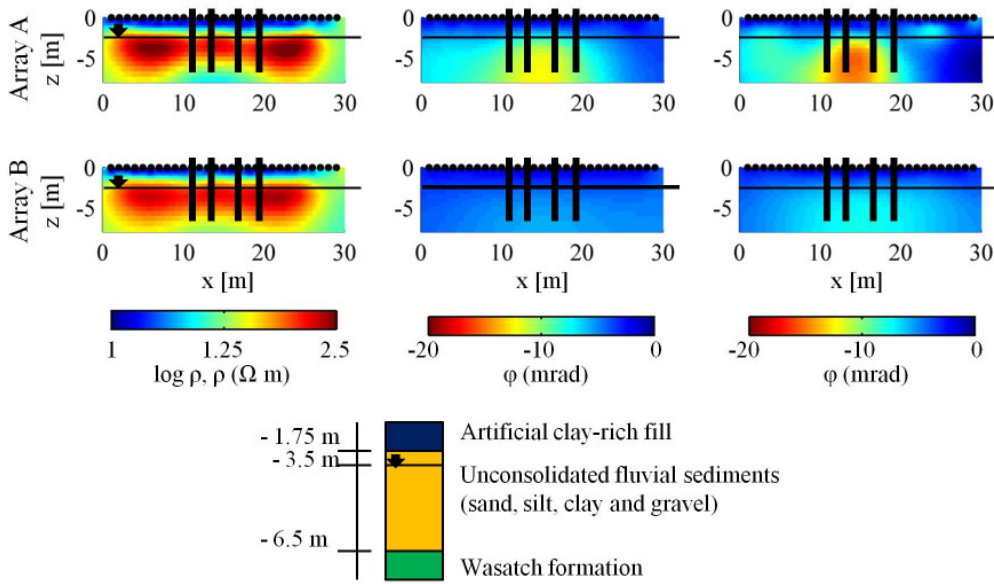


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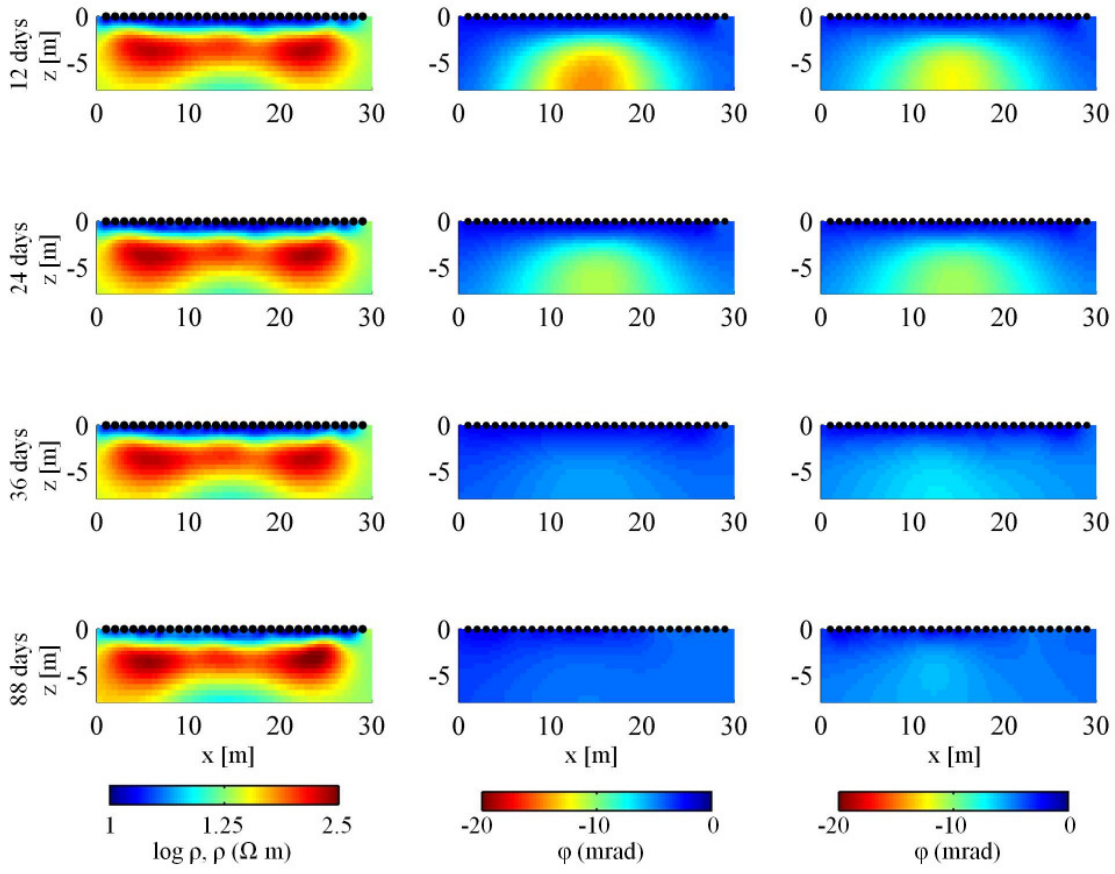


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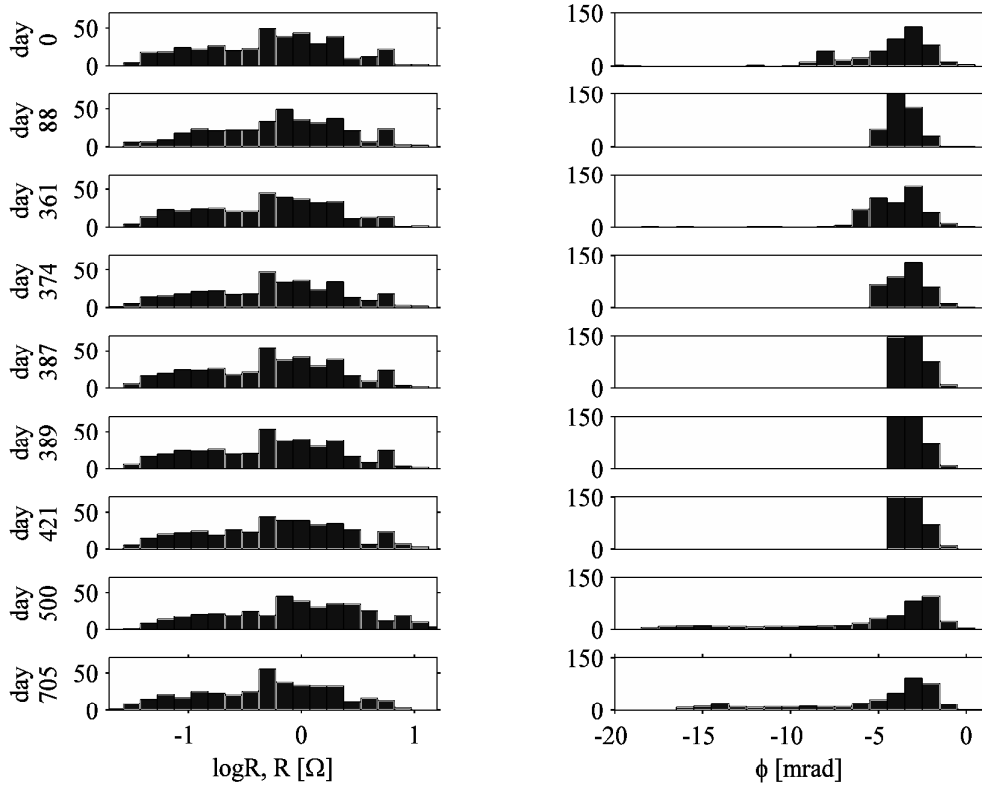


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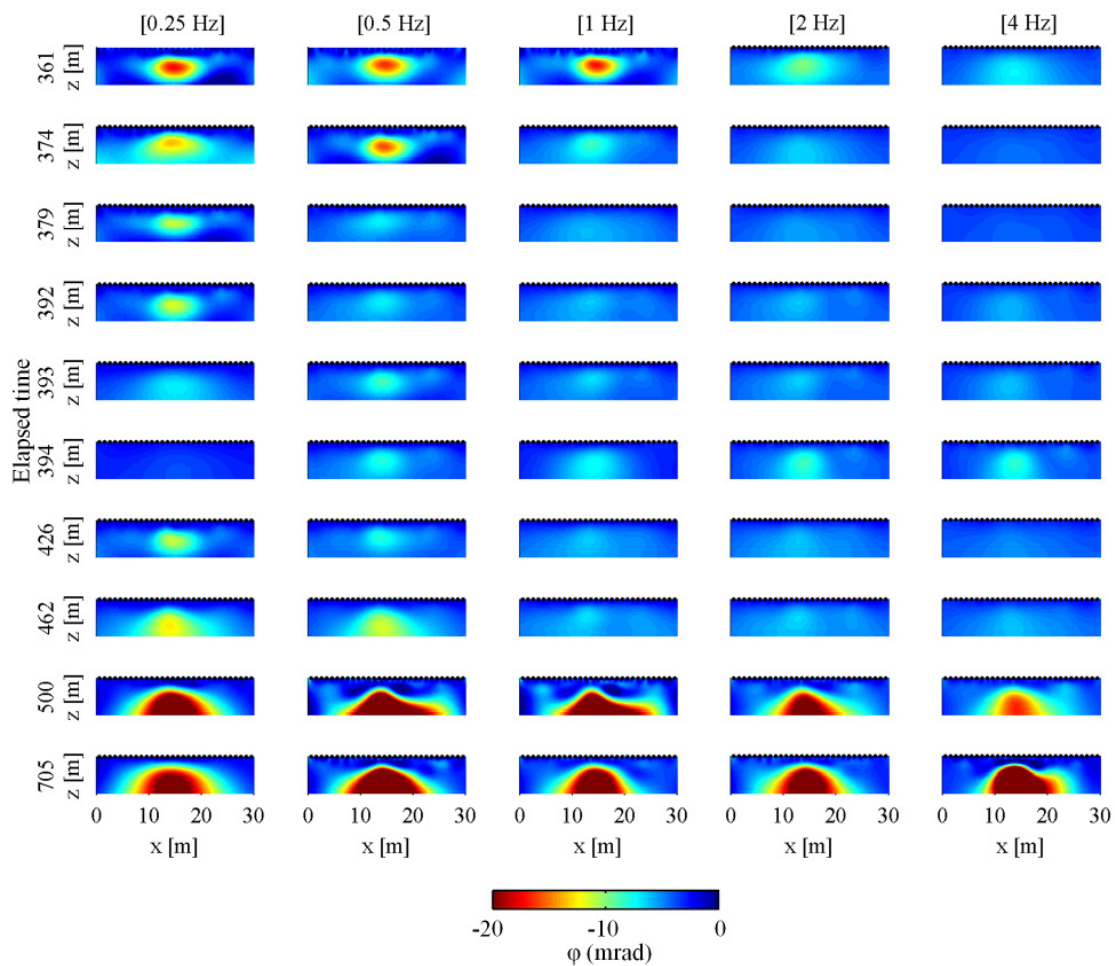


Figure 5: Selected phase images for the data collected at different times and frequencies along array A during 2008-2009. Elapsed time in days is referenced to the start of acetate injection in 2007.

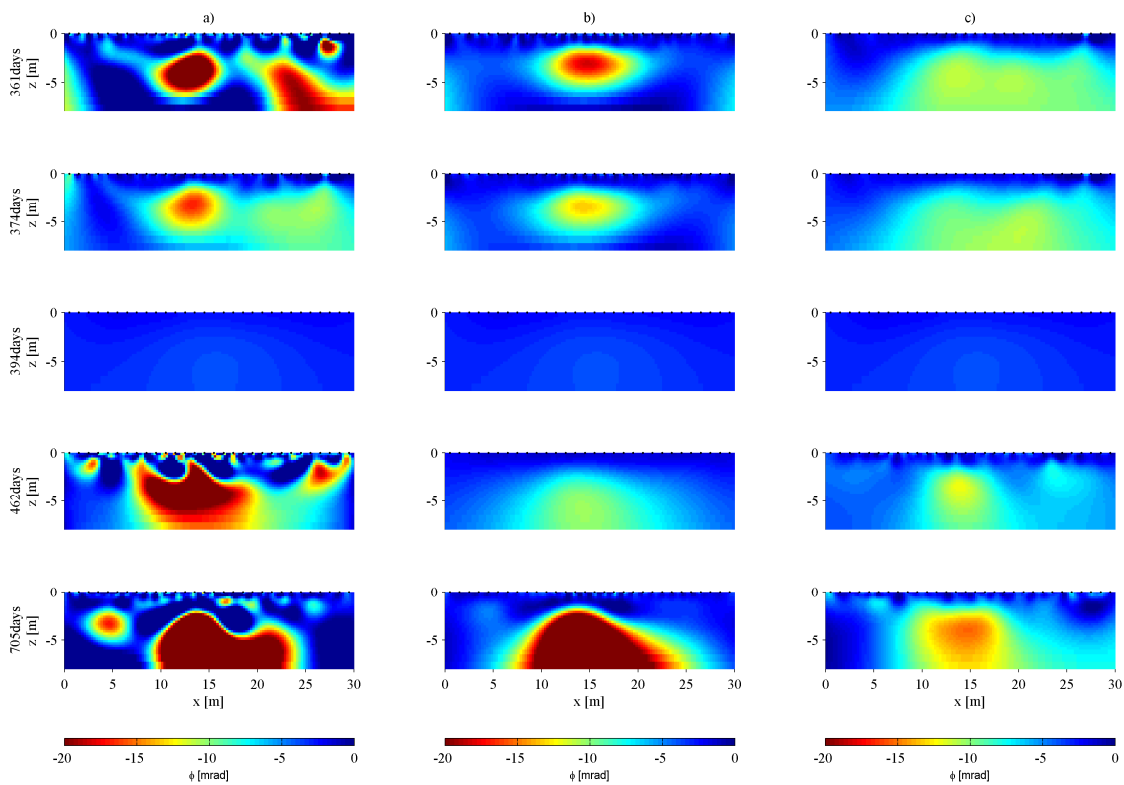


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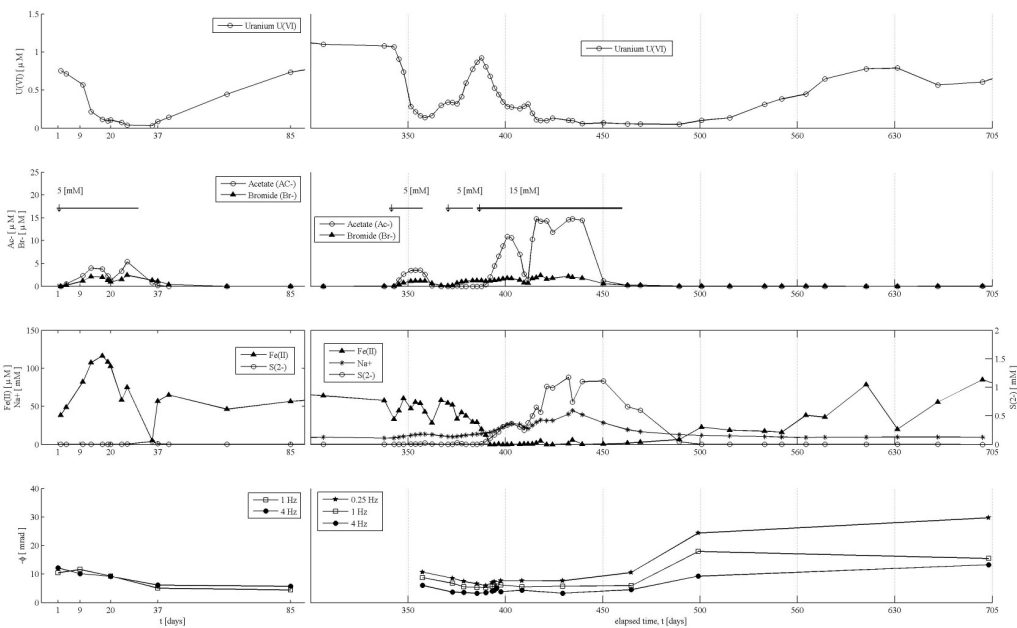


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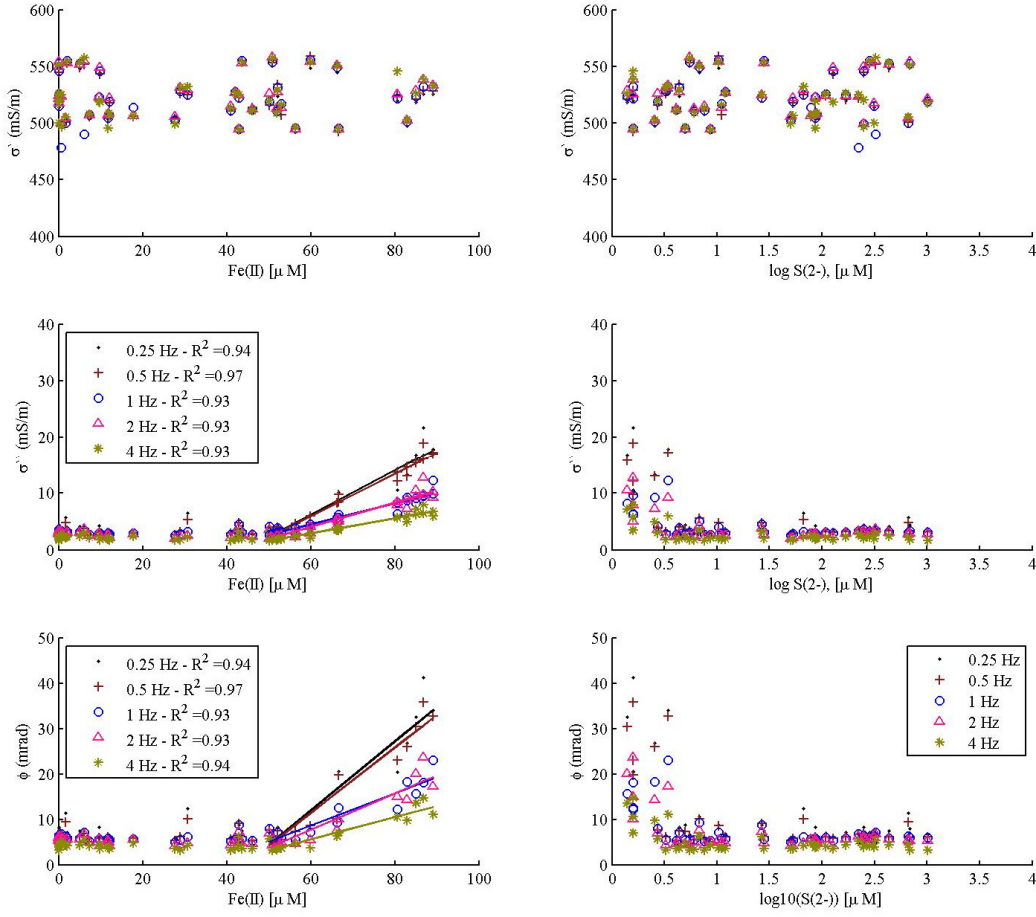


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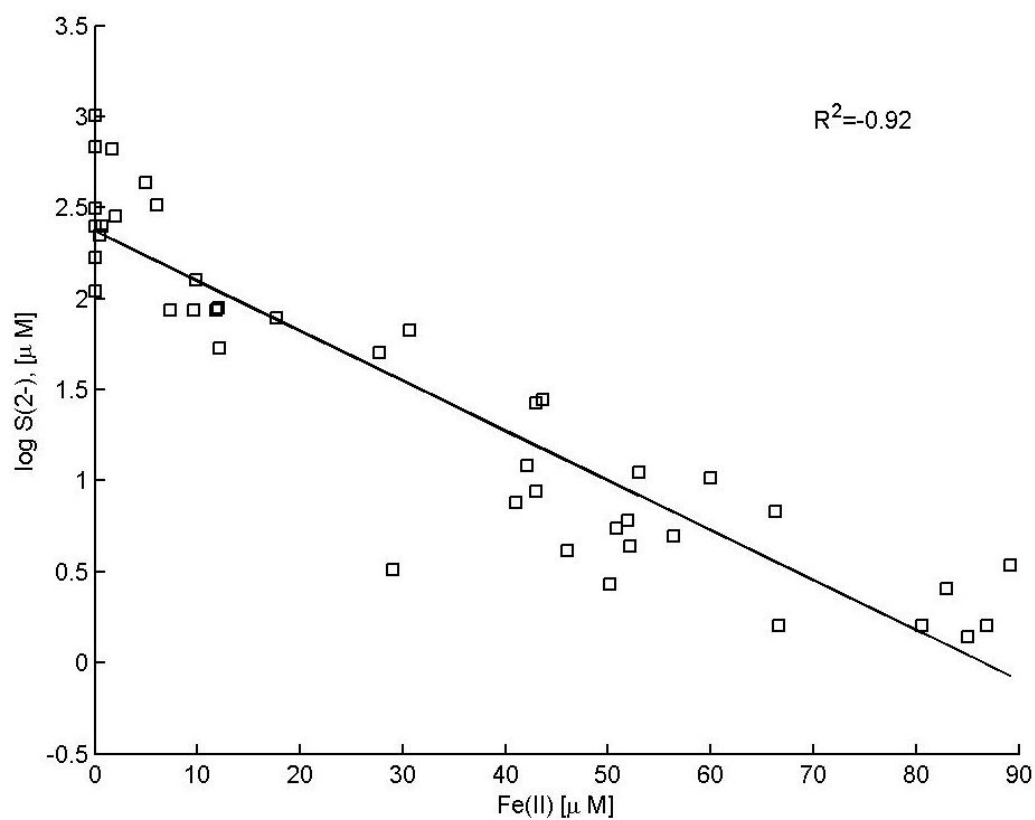


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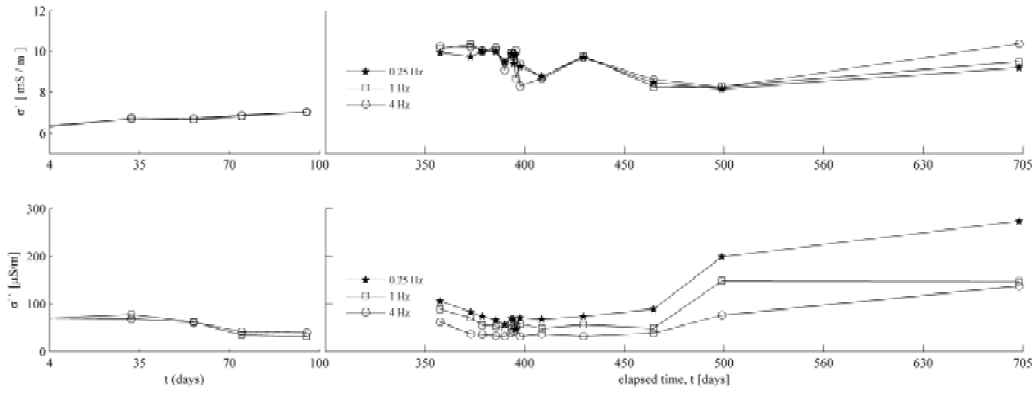


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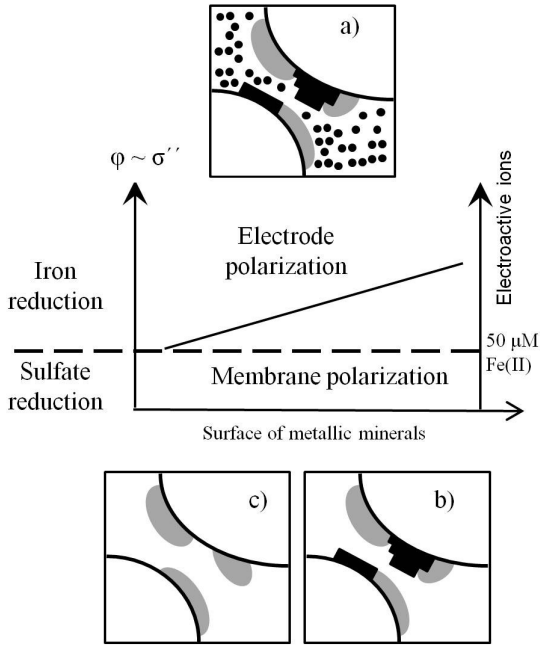


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Year	2007	2008	2008	2008	2008	2008	2008-2009
No. of injection	1	2	3	4	5		-----
Duration [days]	31	15	8	15	6	66	-----
Acetate [mM]	5	5	-----	5	15		-----
Bromide [mM]	2	2	-----	2	2		-----
Meas. Freq. [Hz]	1, 2, 4	0.25 - 4	0.25 - 4	0.25 - 4	0.25 - 4		0.25 - 4
Acquisition period [days]	12	3	3	3	2	30	180

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