## Field-scale time-domain spectral induced polarization monitoring of geochemical changes induced by injected CO<sub>2</sub> in a shallow aquifer

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## ABSTRACT

Contamination of potable groundwater by leaking CO<sub>2</sub> is a potential risk of carbon sequestration. With the help of a field experiment, we investigated whether surface monitoring of direct current (DC) electric resistivity and induced polarization (IP) could detect geochemical changes induced by CO<sub>2</sub> in a shallow aquifer. For this purpose, we injected CO<sub>2</sub> at depths of 5 and 10 m and monitored its migration using 320 electrodes on a  $126 \times 25$  m surface grid. Measured resistances and IP decay curves found a clear signal associated with the injected CO<sub>2</sub> and rebounded to preinjection values after the end of the injection. Full-decay 2D DC-IP inversion was used to invert for the subsurface distribution in Cole-Cole parameters and changes to these parameter fields over time. The time-lapse inversions found

plumes of decreased resistivity and increased normalized chargeability. The two plumes were of different shapes, with the resistivity anomaly being larger. Comparison with measurements of electric conductivity and aluminum (Al) concentrations indicated that two geochemical processes were imaged. We interpreted the change in resistivity to be associated with the increase in free ions directly caused by the dissolution of  $CO_2$ , whereas the change in normalized chargeability was most likely linked to persistent acidification and best indicated by Al concentrations. The results highlight the potential for monitoring of field scale geochemical changes by means of surface DC-IP measurements. Especially the different developments of the DC resistivity and normalized chargeability anomalies and the different associated geochemical processes highlight the added value of IP to resistivity monitoring.

## INTRODUCTION

Geologic carbon sequestration (GCS) is currently considered to be a promising technique to avoid  $CO_2$  emissions from large emitters, such as fossil-fuel power stations. Captured  $CO_2$  could be stored permanently in abandoned oil and gas fields, saline formations or coal beds, or beneath layers of (sealing) impermeable cap rock (Benson et al., 2005). To date, several pilot experiments have successfully demonstrated  $CO_2$  injection into saline formations (Michael et al., 2010), and three larger projects with injection rates of 1-Mt  $CO_2$  per year are currently being operated (Scott et al., 2013). During and after injection of  $CO_2$ , it is important to monitor both the reservoir with the migrating  $CO_2$ , the cap rock, and overlying formations to achieve a safe and efficient operation of underground  $CO_2$  storage (Benson et al., 2005).

The risk of leakage from  $CO_2$  injected underground is driven by the increase in pressure that is inherently caused by the injection as well as buoyancy due to the lower density of the injected  $CO_2$ . The increased pressure can lead to migration of the native saline water or the  $CO_2$  itself into fresh-water aquifers, if the reservoir and aquifer are hydraulically connected. Even if numerical studies found that leakage is extremely unlikely (Nicot, 2008; Birkholzer et al., 2009), monitoring schemes should be in place to detect any change in groundwater quality that is caused by a deep injection.

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One key focus of the GCS research conducted over the past 10 years has been on the effects elicited by CO<sub>2</sub> on water quality in shallow potable aquifers overlying storage reservoirs. The shallow aquifer water chemistry focus can be described broadly as having two main aims: (1) to determine how deleterious a leak may be to groundwater resources and to human health (Siirila et al., 2012) and (2) how leakage can be detected best geochemically (for monitoring purposes) (Klusman, 2011). Numerical modeling (Carroll et al., 2009; Zheng et al., 2012; Navarre-Sitchler et al., 2013), field studies (Spangler et al., 2009; Peter et al., 2012; Trautz et al., 2013; Cahill et al., 2014), and laboratory studies (Little and Jackson, 2010; Cahill et al., 2013) have all been used recently to characterize the likely effects of CO<sub>2</sub> leakage on shallow aquifers. The field studies have shown the effects of CO2 on water chemistry and sediments in real systems, i.e., reduction in pH, dissolution/precipitation of reactive minerals, sorption/desorption processes, and the associated increases in major and minor ions. The field studies have confirmed conclusions drawn from the modeling and laboratory experiments.

Geophysical monitoring can help with the detection and observation of potential leaks. Direct monitoring of water chemistry necessitates extraction of groundwater samples in wells, and typically only a few wells can be installed. Additionally, the drilling locations need to be predefined before the start of an experiment, which in turn requires detailed information about the groundwater flow, which is difficult to obtain. The information about groundwater chemistry is, therefore, typically limited to scarce point measurements. Surface and crosswell geophysical methods can complement these measurements by imaging the subsurface at a scale of tens to hundreds of meters (Rubin and Hubbard, 2005).

Direct current (DC) and induced polarization (IP, complex resistivity) measurements can image the electric structure of the subsurface, which is closely related to the hydrological properties, such as porosity and state variables like salt concentration (see, e.g., Revil et al. [2012c] for a recent review). Surface DC monitoring is minimally invasive, and it has been used in a wide variety of applications, ranging from a water tracer in the vadose zone (Park, 1998), over salt tracers (e.g., Cassiani et al., 2006; Doetsch et al., 2012) to hyporheic exchange (Cardenas and Markowski, 2011) and heat tracers (Hermans et al., 2012).

In environmental studies, IP data have mostly been collected for site characterization, and IP inversion results have been shown to improve the hydrogeologic aquifer characterization (e.g., Slater and Lesmes, 2002; Kemna et al., 2004). The IP signal is sensitive to the pore size (Revil et al., 2014) and structure that controls hydraulic parameters and Binley et al. (2005) and Hördt et al. (2007) show the potential of deriving hydraulic conductivity from IP measurements. The IP data have also been found to be affected by mineral precipitation and geochemical changes caused by microbial activity (e.g., Ntarlagiannis et al., 2005; Williams et al., 2009; Revil et al., 2012a). Dafflon et al. (2013) use laboratory and field IP measurements to test the influence of dissolving CO2 in groundwater. Their laboratory measurements show a decrease of the IP effect with a decrease in pH, and field data show a reduction in the raw IP effect after CO<sub>2</sub> injection, but the experimental setup did not allow for inversions of the IP data

Time-lapse IP surveying and inversion have been proposed for imaging changes in the geochemistry and pore structure (e.g., Karaoulis et al., 2011), but only a few field examples of time-lapse IP imaging exist. Williams et al. (2009) image an increasing IP effect (phase shift) that was caused by biostimulation, in which microorganisms changed groundwater geochemistry and caused sulfide mineral precipitation. Another bioremediation experiment was monitored by Johnson et al. (2010) in 3D, and Flores Orozco et al. (2011) successfully image an acetate injection into a uranium-contaminated aquifer. Flores Orozco et al. (2013) analyze the same uranium contaminated aquifer using time-lapse spectral IP measurements, and find that the time constant and chargeability increase in response to microbial activity.

Whereas these studies analyze a single frequency or the integral chargeability, we here use the full IP decay of time-lapse data. Fiandaca et al. (2012, 2013) implement an IP inversion algorithm that uses all available time gates of a time-domain acquisition to invert for the four parameters of the Cole and Cole (1941) resistivity model (Pelton et al., 1978). In contrast to other inversion algorithms that invert for the integral chargeability or for the phase change at different frequencies independently, the full-decay inversion can capture all frequencies that exist in the gated IP decay curves in four parameter fields. Gazoty et al. (2012) and Fiandaca et al. (2013) invert IP data collected over landfills and find that the Cole-Cole model is necessary to account for the significant frequency variations in the decay curves.

Here, we test if time-lapse DC and IP inversions can image geochemical changes at the field scale. For this purpose, we injected 1600 kg of  $CO_2$  into a shallow silicate aquifer (Cahill et al., 2014), where a pilot study has previously shown that dissolving  $CO_2$  gives a clear signature of increase in electric conductivity (EC) (Cahill and Jakobsen, 2013). Auken et al. (2014b) invert the DC resistance data in 3D and are able to image the plume of dissolved  $CO_2$ . In this study, we concentrate on the main transect along the groundwater flow direction and invert the full IP decays along with the measured resistances. Only a few examples of field-scale time-lapse IP results exist, and this is the first study that uses the full decay. Therefore, processing and inversion steps are described in some detail. Finally, the results are compared with the geochemical analysis of Cahill et al. (2014).

## FIELD SITE AND DATA COLLECTION

## Hydrogeologic setting and CO<sub>2</sub> injection experiment

The CO<sub>2</sub> injection experiment was carried out at Vrøgum plantation near Esbjerg in western Denmark, approximately 6 km from the North Sea coast (Figure 1b). The field site is mostly flat, with only a few sand dunes south of the main area of interest. The area around the CO<sub>2</sub> injection location is open grassland, surrounded by forest at 10–30 m distance. The geology is sand dominated, with aeolian sand in the top 5 m, followed by a 5-m-thick layer of glacial sands. Marine sands are found below 10 m depth (Figure 1a). The groundwater table is at 1.5–2 m depth within the aeolian sand, with a seasonal variation of approximately  $\pm 0.5$  m. The hydraulic gradient is quite stable at 0.0014, falling toward the south–southwest.

The layout and design of the  $CO_2$  injection were planned on the basis of a pilot study with a 45 kg  $CO_2$  injection in 48 h (Cahill and Jakobsen, 2013). In the main experiment,  $CO_2$  was injected in two screened intervals at 4–5 and 9–10 m depth in two wells separated horizontally by 2 m and arranged to create a curtain of  $CO_2$  perpendicular to the groundwater flow direction (Cahill et al., 2014). Injection was started on 14 May 2012, and all time references are given with respect to this date. The initial injection rate of food-quality gas

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phase CO<sub>2</sub> was 12 L/min. After 14 days of injection, dry groundwater sampling points indicated desaturation, and the initial injection rate was therefore reduced to 6 L/min (16 kg CO<sub>2</sub>/day). This injection rate was maintained until 24 July, with the total amount of injected CO<sub>2</sub> adding up to 1600 kg in 72 days.

#### Electrical monitoring setup and data acquisition

Five parallel profiles with 64 electrodes each (320 electrodes total) were installed at a crossline spacing of 5 or 8 m parallel to the groundwater flow (see Figure 1 in Auken et al., 2014b). The electrodes were installed at 2 m inline spacing, and contact resistances were reduced by embedding the steel electrodes in bentonite. The steel electrodes were connected to an Iris Instruments Syscal® resistivity meter using multicore cables and custom-designed switch boxes. The switch boxes allowed for 2D measurements along each profile and 3D measurements across the lines (Auken et al., 2014b). The acquisition and monitoring system were designed for minimum user interaction and included a gasoline-powered electricity generator, four car batteries, a field computer, and wireless communication. The system could be remotely controlled, and data were uploaded automatically into an online database (see Auken et al. [2014b] for details about the installed system).

Acquisition of DC and full-decay IP data was started on 27 April 2012, so that 17 days of baseline data could be acquired before the beginning of the  $CO_2$  injection. Continuous acquisition was planned for the entire experiment, but problems with the acquisition system (e.g., unstable communication and problems with the power supply) caused several interruptions in the acquisition. Nevertheless, good-quality data are available for the 120 days following the start of the  $CO_2$  injection. Auken et al. (2014b) process and invert the DC component of this complete data set, and invert for the 3D resistivity distribution and its change over time. Here, we concentrate on the central 2D profile, running through the injection point. This central profile runs in the groundwater flow direction, and results of the 3D DC inversions as well as the water samples (Auken et al., 2014b) show that the main  $CO_2$  pulse follows the direction of this profile.

The acquired four-electrode configurations on the central profile consisted of gradient-type measurements, with a current electrode spacing of 12–48 electrodes (24–96 m) and a potential electrode spacing of 1–4 electrodes (2–8 m). All configurations were optimized to use the 10-channel capability of the resistivity meter. The 61 data sets were acquired within 120 days after the start of the  $CO_2$  injection, and each data set contains 886 four-electrode configurations.

## Geochemical water sampling

Cahill et al. (2014) plan and implement an extensive groundwater sampling campaign that was targeted at measuring and understanding the hydrogeochemical and mineralogical effects of the sustained  $CO_2$  contamination at the site. The 13 wells with 33 sampling points were installed on the main transect; that is, they were collocated with the central electrode profile. Most of the sampling points were located at 4 and 8 m depth, with some additional ones at 2, 6, and 10 m depth (see Figure 1c). Sampling at regular time intervals was started before the start of the  $CO_2$  injection and continued throughout the experiment until 252 days after the injection start.

Water chemistry at each sampling location was monitored for EC, pH, and dissolved element evolution (Ca, Mg, Na, Si, Ba, Sr, Al,

Zn, Mn, Fe, and K). Cahill et al. (2014) find that the injected CO<sub>2</sub> first causes an advective elevated ion pulse, which is followed by increasing persistent acidification. The ion pulse is characterized through an increase of the groundwater EC, which can be observed at most sampling points. In the pilot study (Cahill and Jakobsen, 2013) and in the main experiment (Cahill et al., 2014), EC is found to be the best indicator for dissolved CO2 in the groundwater. Most dissolved element concentrations are found either to develop with the advective pulse or to show a strong pH-dependent behavior (Cahill et al., 2014). Aluminum (Al) is found to exceed WHO guidelines by a factor of 10, whereas all other element concentrations remain significantly below guideline limits. Here, the comprehensive geochemical data enable assessment of the DC and IP inversion results. The changes in DC resistivity can be compared with and validated with the changes in EC (see also Auken et al., 2014b). The link between changes in geochemistry and polarization effects is more complex and is the subject of active research (e.g., Vaudelet et al., 2011a, 2011b; Revil et al., 2013). Comparison of the geochemical data with the IP inversion results can give insights into these effects and their detectability on the field scale.

## INDUCED POLARIZATION DATA PROCESSING AND INVERSION METHODOLOGY

#### Processing of induced polarization decay curves

The DC and IP measurements were recorded using a square waveform with a 2 s on and 2 s off time. This waveform was repeated twice for each four-point configuration (stacking of two) to reduce the measurement noise. The applied voltage between the current electrodes was 400 V for all measurements, and the injected current varied between 50 and 300 mA (mean of 150 mA) as a function of electrode contact resistance. For each of the 886 four-point configurations in each data set, the instrument recorded the DC voltage and the transient IP decay after switching the current off. The IP decays



Figure 1. Field site and experiment layout: (a) 64 electrodes were installed along a profile at a field site located close to (b) the west coast of Denmark. Local geology consists of different sands, with the groundwater table at 2 m depth. (c)  $CO_2$  was injected at 5 and 10 m depths, and water samples were retrieved at 33 locations in boreholes.

were recorded in 20 gates, with integration times starting at 20 ms and the last gate being centered at 1700 ms. The individual gate length increased logarithmically with time starting at 10 ms and ending at 350 ms.

The repeated measurements over a long period of time made it possible to assess the repeatability of the IP measurements. Based on this assessment and physical plausibility, decays were removed where IP gate values were negative, more than 500 mV/V or where the decay curve was increasing. Additionally, some decay curves were manually removed because they were clearly erroneous and possibly effected by coupling (e.g., high value for last gates and very low value for first gates). Most removed data were acquired at the sand dune toward the southern end of the profile (x = 40 - 65 m), where coupling was poor, due to the dry sand at the surface. A low-pass filter that is built into the hardware of the resistivity meter contaminated the first three gates of all decay curves. Although we account for this filter effect in the forward modeling (Fiandaca et al., 2013), a bias effect is noticeable if the filter description is just slightly inaccurate. Considering that the instrument was repaired and finally substituted during the experiment, we decided to remove these gates to avoid inversion bias due to improper filter description.

The processed data set includes 634 of the initial 886 four-electrode configurations that were measured 61 times during the experiment, and each data point consists of a DC resistivity measurement and a high-quality IP decay with 17 gates, with midpoints ranging



Figure 2. Sample IP decays for different focus depths around the injection point. Each panel shows IP decay curves for three acquisition times: preinjection (day 0), during  $CO_2$  injection (day 39), and after the injection (day 114). The estimated errors (shown for day 0) are estimated for each reading, based on the measured voltage.

from 55 to 1700 ms. Figure 2 shows some typical decays for measurements with four different focus depths, centered around the injection well. The measurement errors for DC and IP values were estimated as a combination of an absolute measurement uncertainty of 0.2 mV in the voltage measurement and a relative error contribution. For the DC measurements, the relative error was estimated as 4% for the baseline data set and 2% for the time-lapse inversion. For the IP readings, the same relative error contribution of 4% was used for all measurements. The resulting mean errors were 4.1% for the DC baseline data set, 8% (1.8 mV/V) on the first IP gate, and 20% (1.3 mV/V) on the last IP gate. The seemingly high relative error on the last IP gate is a result of the low signal level at the end of the decay. Further details about the estimation of the data errors are given in the paragraph describing the time-lapse inversion.

The decays for three different acquisition days in Figure 2 illustrate the clear change of the IP decays during the injection and its rebound to preinjection values after termination of the injection. Especially electrode configurations with focus points at shallow depths around the injection wells show a clear response to the injected  $CO_2$ . Figure 2 also shows the increase of the estimated IP errors with focus depth and the more noisy appearance of deepsensing decays. This error increase is due to the smaller measured voltages for large electrode separations that are needed for sensing the deeper underground. Because the deepest  $CO_2$  injection is at a depth of 10 m, an effect of the  $CO_2$  injection at a focus depth of 14 m should be negligible.

## **Cole-Cole parameterization**

Inversion of time-domain full-decay IP data (Fiandaca et al., 2012, 2013) uses the decay information along with the DC measurements to invert for parameter distributions that explain the measured data. Extra inversion parameters in addition to resistivity are necessary to describe the subsurface polarization and its frequency dependence, and several models have been suggested in the literature. For example, the constant phase angle model (Van Voorhis et al., 1973; Börner et al., 1996) parameterizes the IP effect using one parameter that describes the constant phase shift in the frequency domain, and it is proportional to the integral chargeability in the time domain. Although capable of fitting most laboratory measurements, the constant phase angle limits the shape of the decay curves to the shape of a power function, at least for the homogeneous case. However, most measured decays from our field site show more complicated decays. Power functions plot as straight lines in log-log plots, which is not the case for the decays of Figure 2. Other data that are not shown deviate even more from the constant phase model.

Here, we prefer to use the Cole and Cole (1941) resistivity model (Pelton et al., 1978) that uses four parameters to characterize the soil impedance and describes a wider range of decay types. It has been widely applied in time-domain IP inversions (e.g., Yuval and Oldenburg, 1997; Hönig and Tezkan, 2007) and spectral IP analysis (e.g., Yoshioka and Zhdanov, 2005; Loke et al., 2006). Nevertheless, the flexibility of the Cole-Cole model in fitting decay curves comes at the cost of a possible nonuniqueness of the four parameters or of poorly resolved parameter fields, particularly for values of the time constant smaller than the first time gate used in the decay measurement (Ghorbani et al., 2007; Fiandaca et al., 2012). Especially in the case of noisy field data, not all four parameters can be expected to be fully resolved in all parts of the model. It is therefore a choice

of assuming a less-flexible decay type (e.g., constant phase model) or allowing more freedom, but having some of the parameters controlled by regularization in the inversion. Here, we choose the second option and use the Cole-Cole model with regularization on the four parameters.

We parameterize the complex resistivity  $\zeta_j$  in each cell *j* in the 2D parameter mesh as (Pelton et al., 1978)

$$\zeta_{j}(\omega) = \rho_{i} \left[ 1 - m_{0_{j}} \left( 1 - \frac{1}{1 + (i\omega\tau_{j})^{c_{j}}} \right) \right], \qquad (1)$$

where  $\rho$  is the DC resistivity,  $m_0$  is the intrinsic chargeability,  $\tau$  is the time constant, c is the frequency exponent, and i is the imaginary unit. In the combined DC-IP inversions, we invert for all four parameters simultaneously.

Nonmetallic polarization at low frequencies ( $\leq 1000 \text{ kHz}$ ) results from diffusion controlled polarization processes at the interface between the mineral surfaces and the pore solution. This surfacecontrolled polarization can be represented by a complex conductivity  $\sigma$  (Lesmes and Frey, 2001; Slater and Lesmes, 2002):

$$\sigma = \sigma_{bulk} + \sigma'_{\text{surf}}(\omega) + i\sigma''_{\text{surf}}(\omega), \qquad (2)$$

where  $\sigma'_{\text{surf}}$  and  $\sigma''_{\text{surf}}$  represent the real and imaginary surface conductivity,  $\sigma_{\text{bulk}}$  is a bulk conduction term acting in parallel to the surface conduction, and *i* is the imaginary unit. For the Cole-Cole resistivity model of equation 1, the surface quadrature conductivity  $\sigma''_{\text{surf}}$  is proportional to  $m_0/\rho$  (considering  $\sigma_{\text{bulk}} = 1/\rho$ ). Consequently, in addition to the four Cole-Cole parameter fields, in the following we also plot and analyze the normalized chargeability  $m_0/\rho$  because it is closely related to lithology (through the specific surface area) and surface chemistry.

# Sensitivity of induced polarization decays to Cole-Cole parameters

To assess the sensitivity of the IP decays to variations in the Cole-Cole parameters and to judge if it is possible to resolve these variations, we calculate several exemplary decay curves shown in Figure 3. The baseline decay (solid black line) uses parameters that are typical for our field study ( $m_0 = 25 \text{ mV/V}$ ,  $\tau = 0.8 \text{ s}$ , and c = 0.7). The three dashed lines show IP decay curves that represent 20% reductions in each of the three parameters, while keeping the other two parameters at their baseline value. The change in  $m_0$  acts as a shift to the decay curve (in logarithmic space; in linear space it would be a factor), whereas the changes in  $\tau$  and c change the shape of the curve. The assumed errors on the baseline decay curves are the same as on the 4-m focus depth example in Figure 2b.

Figure 3 illustrates that only the 20% decrease in  $m_0$  causes a significant change in the decay curve that is larger than the assumed error. This visual impression is confirmed when calculating the normalized data difference (misfit) of the three varied curves with respect to the baseline decay: The misfit is 0.73 and 0.71 when varying  $\tau$  and c, and it is 2.16 when varying  $m_0$  by 20%. This means that the modeled decay curves with 20% change in  $\tau$  and c are still within the assumed data error, but the change in  $m_0$  does create a clear signal. Consequently, we can expect to resolve 10%–20% changes in  $m_0$  and  $\rho$  (that is independent of this decay curve analysis), but bigger relative variations in  $\tau$  and c are necessary to cause a significant variation of the DC-IP signal.

## DIRECT CURRENT-INDUCED POLARIZATION INVERSIONS AND RESULTS

## **Baseline inversion**

All DC-IP data were inverted using the 2D forward modeling and inversion algorithm embedded in AarhusInv (Fiandaca et al., 2012, 2013; Auken et al., 2014a), where the DC-IP models are parameterized using the above described Cole-Cole model. The full-decay IP forward modeling functionality uses Cole-Cole parameter fields, calculates the complex resistivity distribution at different frequencies, and calculates the forward responses at these frequencies (typically 10 frequencies per decade). These forward responses are then combined and transformed to time domain using fast Hankel transforms. Details of the forward modeling are described in Fiandaca et al. (2013). The parameter mesh for the inversion is built using the global-positioning-system-derived topography and electrode positions, with a lateral cell spacing of 1 m, which corresponds to half the electrode spacing. Vertical discretization was chosen to include 19 layers, with a layer thickness of 0.5 m at the surface and increasing thickness with depth. This parameter mesh is refined in the forward modeling, for increased accuracy.

We first invert a baseline data set that was acquired a few hours before the CO<sub>2</sub> injection started on 14 May 2012. A homogeneous starting model was chosen for all parameters, with  $\rho = 480 \ \Omega m$ ,  $m_0 = 5 \ mV/V$ ,  $\tau = 1.0 \ s$ , and c = 0.5. Horizontal and vertical first-order smoothing were chosen as model regularization, with no damping toward the starting model. The horizontal smoothing operates laterally with respect to elevation (not depth below surface), assuming a standard deviation of 7.5%. The assumed variation in the vertical direction is somewhat larger, with a standard deviation of 25%. The same regularization was used for all four Cole-Cole parameter models.

In the combined inversion of DC and IP data, the relative weight of each data set needs to be carefully considered and tested, to ensure reliable and stable convergence. The number of IP data points is much larger than the number of DC readings because for each DC measurement, a full IP decay with 17 samples is included in the inversion. These IP measurements are naturally strongly correlated because they belong to the same decay. The extra information contained in the IP data is therefore considerably less than the extra number of data points suggests, and the IP data may need to be down weighted to ensure a balanced fit of DC and IP measurements. The weighting of each data point in the inversion is realized through misfit normalization using the estimated errors. Due to the lower



Figure 3. Analysis of IP decay sensitivity to a 20% decrease in individual Cole-Cole parameters. Each parameter was decreased, whereas the others remain at their baseline values. Only the 20% decrease in  $m_0$  results in an IP decay curve outside the typical error bounds and can thus be resolved in an inversion.

signal level, these estimated errors are higher for the IP measurements (8%–20%) than for their DC counterparts (4%, see the subsection "Preprocessing of IP decay curves"). These lower error estimates give a stronger weight to the DC data and help the stability of the inversion. Two additional measures were tested to help the convergence of the inversion and reduce the risk of prematurely stopping the inversion in a local minimum: (1) reducing the weight of the IP data in the optimization by a factor of two and (2) first inverting the DC data only, before adding the IP data in a combined inversion. Both settings give similar results, and we choose here to follow the second approach, in which the DC-only inversion result is the basis for the combined inversion. Using this sequential approach, we find that although the IP data misfit decreases monotonously in the combined inversion, the already low DC data misfit increases first and then decreases again, when the IP data are also



Figure 4. (a-d) Four Cole-Cole parameter fields for the baseline inversion result, along with the (e) normalized chargeability  $m_0/\rho$  field and (f) data misfit. The resistivity  $\rho$  section (a) shows high resistivities in the unsaturated zone, intermediate resistivities in the glacial sands, and low resistivities in the marine sands below 10 m depth. Normalized chargeability  $m_0/\rho$  (e) shows very low values (<0.02 mS/m) in the unsaturated sand dune (x > 40 m) and otherwise relatively low values approximately 0.1 mS/m, and (f) shows the data misfit along the profile for the DC (blue) and IP (red) measurements.

close to a normalized data misfit of  $\chi = 1$ . The final DC data misfit is generally 20%–30% higher than that of DC-only inversions.

The preinjection baseline inversion result in Figure 4 converged to a final normalized data misfit of  $\chi = 0.78$  in four DC-only iterations and seven iterations combining DC and IP data. The data misfit plot in Figure 4f shows that the data are explained fully in the central part of the profile and high data misfits only occur toward the ends of the profile, especially near the sand dune between x = 40 - 70 m. The resistivity model in Figure 4a confirms the general geology at the site. The unsaturated aeolian sand above 13 m elevation (2 m depth at the center of the profile) is characterized by high resistivities of more than 600  $\Omega$ m. The sand dune at approximately x = 40 - 70 m shows resistivities of more than 1000  $\Omega$ m, which also explains the poor coupling conditions that caused poor data quality in this region of the profile. A layer of

intermediate resistivities that characterize the saturated aquifer with aeolian and glacial sands follows the high-resistivity layer. The lowest resistivities (< 200  $\Omega$ m) are found in the marine sands below 5 m elevation.

The chargeability  $m_0$  and the normalized chargeability  $m_0/\rho$  sections in Figure 4b and 4e show generally small values below 100 mV/V and 0.2 mS/m, respectively, as expected in this sandy geology. The aeolian sand within the dune is found to have very low polarization properties  $(m_0/\rho < 0.02 \text{ mS/m})$ , as expected for unsaturated clean sands. Within the saturated aquifer region, there is some variability in  $m_0/\rho$  that is most likely related to silt lenses within the glacial sands. These heterogeneities were also found when drilling the observation wells. The  $\tau$  section (Figure 4c) shows intermediate decay times of ~0.8 s in the saturated glacial sands and shorter decay times in the shallow aeolian sands. These differences are probably related to the different grain and pore sizes. In fact, the relaxation time increases with grain size (see Binley et al., 2005), and it is even more related to the pore size (Revil et al., 2012b). The pore-size distribution is not available for our sand samples, but the grain size distribution is analyzed by Cahill et al. (2014). The aeolian sand has small grain sizes of 192-367 µm (Cahill et al., 2014) and thus short IP decay times, whereas the glacial sand has grain sizes of 247-589 µm that lead to longer decay times (see Binley et al., 2005). The shorter decay times in the shallow soil could also be caused by the reduced water content (Binley et al., 2005). The frequency exponent (Figure 4d) is mostly in the range of c = 0.2 - 0.5 and shows some variation within the saturated aquifer, but the strongest anomalies are located in the shallow part. These anomalies show low c values, which correspond to a broader frequency spectrum, caused by aeolian and glacial sands with different relaxation times influencing the data in this region. Revil et al (2014) find that c is generally not much more than 0.5, which indicates that the high *c* values at approximately x = 40 m may be unrealistic and possibly artifacts due to the poor data quality (high data misfit) in this part of the profile.

## **Time-lapse inversions**

For the inversion of the time-lapse data that were acquired during and after the  $CO_2$  injection, we select four DC-IP data sets close to the times of the geochemical water sampling. These data sets contain 634 resistance measurements, each with 17 IP decay gates for each resistance measurement. Whereas the baseline inversion aims at imaging the electric properties of the subsurface geologic material, the time-lapse inversions target changes to these subsurface properties over time. In most monitoring experiments, these time-lapse variations are much smaller than electric property differences between geologic units. It is therefore crucial to adapt the processing and inversion settings to target small changes.

#### Time-lapse data correction

For time-lapse DC inversions, it is most common to invert the ratios of the time-lapse and the baseline data (Daily et al., 1992) or to invert the differences in the data (LaBrecque and Yang, 2001). In contrast to time-lapse DC inversions, IP monitoring is a new field of research and only few examples (Williams et al., 2009; Johnson et al., 2010; Flores Orozco et al., 2011) of field scale time-lapse IP inversions exist. Karaoulis et al. (2011) develop an algorithm for 3D time-lapse IP inversions and demonstrate their approach on synthetic data, but results from field studies using their approach are currently outstanding. The above-mentioned studies either solve for the IP phase shift at individual frequencies or analyze the integral chargeability.

This study is the first to invert the full IP decay curves for a timelapse data set. We therefore evaluated if time-lapse correction of the IP data is beneficial. We tested an approach that is analogous to the DC data correction in equation 2 of Doetsch et al. (2012), where the IP data  $M_{ij}$  of time step *i* and gate number *j* are corrected for the baseline misfit, so that the inverted chargeabilities are

$$\tilde{\mathbf{M}}_{ij} = \frac{\mathbf{M}_{ij}}{\mathbf{M}_{0j}} g(\mathbf{m}_{bg}, j), \tag{3}$$

where  $g(\mathbf{m}_{bg}, j)$  denotes the forward operator for the baseline model  $\mathbf{m}_{bg}$  and gate j and  $M_{0j}$  are the baseline data set of IP gate j. This correction adjusts the data, so that only relative changes to the baseline data are inverted. The correction acts on the individual time gates, which is convenient to implement, but it may create problems if the baseline decay curves are noisy. Other correction approaches are possible, in which the changes in the full decays are analyzed. However, such approaches require fitting of the IP decay curve; e.g., to a multiexponential decay, which creates additional complications. We therefore only test the IP data correction of equation 3.

The inversion tests using the correction on the DC and the IP data gave good results, and it was possible to assume smaller IP data errors than when using the raw IP data. The inversion results were, however, practically identical to inversions without the correction. This indicates that the static error contribution that is the same in all IP data is much smaller than for DC data. The static DC error is largely due to uncertain electrode positions and inaccuracies in the forward modeling. The most likely reason for the small static IP error is that IP data are not strongly affected by geometric errors. Although electrodepositioning errors strongly influence DC data, the decay curves are normalized by DC voltages, and therefore the effect of geometric errors is much smaller. The IP data are, however, also indirectly influenced by geometric errors through the resistivity distribution. Due to the negligible improvement of using the correction, we decide to use the uncorrected raw data  $M_{ij}$  in the inversions. Consequently, timelapse data correction was performed on the DC data only, in the same way as for the 3D inversions of the DC data that were collected during the same CO<sub>2</sub> injection experiment (Auken et al., 2014b).

#### Error estimation

We test three approaches for estimating the error on the IP measurements. The simplest was a uniform relative error. This error works well for the first gates (high apparent chargeabilities), but strongly overweighs the tails of the curves with small apparent chargeabilities and thus small error estimates. In cases with chargeabilities approaching zero, it can even cause the inversion to fail completely. For this reason, we also test absolute errors. An absolute error on the normalized chargeabilities (e.g., 1 mV/V) fixes the singularity problem for very small chargeabilities, and it gives a more balanced weight between early and late gates. However, it does not take into account the actual measured voltage between the potential electrodes that has a strong effect on the measurement quality. We therefore use the actual measured voltage to estimate an absolute voltage error (e.g., 0.2 mV). This absolute voltage error gives a good balance between early and late time gates, and it also gives less weight to deeper sensing configurations that have an intrinsically lower signal and higher noise level (see also Gazoty et al., 2013). For the time-lapse data, we use a combination of a 4% relative error contribution and an absolute voltage error of 0.2 mV, which appropriately describes the noise-related variation in our measured data. The error level was here chosen by visually analyzing a large number of decay curves along with the error bars created by the different error models. We find that the inversions are very sensitive to the type of error (i.e., relative versus absolute), but robust against small changes to the assumed error, as long as a combination of relative and absolute voltage error is chosen.

#### Regularization

To resolve small changes to the subsurface properties, it is important to consider the baseline inversion result in the time-lapse regularization. We choose the baseline inversion result as the start and reference model for all time-lapse inversions and invert for the difference to this baseline model. In some applications, it is preferable to use the previous time step as the reference (e.g., Karaoulis et al., 2011), whereas others — especially those using tracers — give best results when using the same baseline model as reference for all time steps (e.g., Doetsch et al., 2010). Here, we use the same preinjection reference model of Figure 4 for all time steps. In the time-lapse inversions, we use a combined regularization, penalizing deviations from the baseline (a priori) model, and the first-order smoothing that was used for the baseline inversions.

Initial tests showed that only changes in resistivity and chargeability were sufficient to describe the DC-IP data variability of the monitoring experiment. This agrees with the above-described analysis on the sensitivity of IP decays to Cole-Cole parameters. The time-lapse inversion results show little change from the base-

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line for  $\tau$  and *c*, when using the same regularization strength for all four Cole-Cole parameters (Figure 5c and 5d). When loosening the a priori constraints on  $\tau$  and *c*, the models show more structure, but without improving the data misfit or showing relevant features. We therefore concentrate on resolving and analyzing the resistivity and chargeability anomalies.

#### Inversion results

Figure 5 shows the four Cole-Cole parameter fields for the timelapse inversion of data collected 39 days after the beginning of the CO<sub>2</sub> injection experiment, along with normalized chargeability  $m_0/\rho$ . The plots show the ratio of the time-lapse inversion result and the baseline model. Values less than one thus indicate a decrease, and values more than one indicate an increase in the respective parameter compared with the preinjection situation. The resistivity



Figure 5. Time-lapse inversion result for day 39 after the beginning of CO<sub>2</sub> injection, shown as ratios with respect to the baseline result. The CO<sub>2</sub>-induced changes are most evident in the (a)  $\rho$ , (b)  $m_0$  and (e)  $m_0/\rho$  sections, along with some near-surface anomalies due to changes in water saturation above the groundwater table. Slight changes in  $\tau$  (c) and c (d) may exist, but they are not necessary to fit the data. The black rectangle indicates the magnified area for Figure 7, and (f) shows the data misfit along the profile for the DC (blue) and IP (red) measurements.

 $\rho$  section (Figure 5a) shows a clear decrease at the injection wells and a little downstream (toward higher x) of the injection. At most other places close to the surface, the resistivity section shows a strong increase in resistivity. This increase in resistivity is due to a decrease in the water table and moisture content of the unsaturated zone. Already small variations (5%) in moisture content due to precipitation events and drying can cause a large (30%) variation in resistivity. Chargeability  $m_0$  (Figure 5b) shows a decrease above the injection points that is similar (in shape and magnitude) to the decrease in resistivity. Comparison with the normalized chargeability section (Figure 5e) shows that this decrease in chargeability is an effect of the decrease in resistivity (i.e.,  $\sigma''_{surf} \propto m_0/\rho$  is constant). But around the shallow injection point, the resistivity decreases more strongly than chargeability, which results in an increase in normalized chargeability around the injection point. At other places, the normalized chargeability changes are bigger than the resistivity ones because  $m_0$  de-

> creases where  $\rho$  increases, for instance close to the surface along the profile. In comparison, the  $\tau$  and c sections show little variation, as discussed above.

> The IP data fit of the baseline inversion and the time-lapse inversion of day 39 can be judged from the measured data and forward modeled decay curves in Figure 6. The forward modeled data explain the measurements to the estimated error level, with the assumed error increasing with depth due to the absolute voltage error contribution. Only the shallow-sensing configurations (Figure 6a and 6b) see a significant change in the IP decay curve over time, and these changes are fully reflected in the forward modeled curves. The decay curves of the deeper-sensing configurations only show variations smaller than the error level. We can, therefore, not expect the  $CO_2$ plume and associated geochemical changes to be fully imaged in the deeper part of the aquifer. Reducing the error level for these deeper sensing configurations would be the key to increase resolution at depth. Possibilities would be to increase the stacking for each measurement or to use an acquisition system with a higher power output or different noise characteristics.

> The time-lapse inversions for days 53, 77, and 114 after the start of the CO<sub>2</sub> injection used the same parameters as discussed for day 39, and all of these inversions fit the data to the assumed error level. Figure 7 shows the resistivity and normalized chargeability sections for the main zone of interest (black rectangle in Figure 5a). The parameters  $\tau$  and c were included in the inversions, but exhibit very little variation and are not shown. The resistivity models (left column in Figure 7) show a developing low-resistivity anomaly that initiates at the injection wells (at x = 0), grows over time, and moves in the direction of the groundwater flow (toward higher x). This anomaly of reduced resistivity agrees well with the low-resistivity anomaly that was imaged in the 3D inversions of Auken et al. (2014b). The

normalized chargeability sections (right column in Figure 7) show an increasing polarizability around the shallow injection point at day 39. At later times, the images show a stronger increase in normalized chargeability of 50%, which extends downstream of the injection wells (toward higher x). The imaged increase in normalized chargeability is relatively shallow, most likely because the deeper part of the aquifer is not resolved. There are also some near-surface anomalies in all resistivity and normalized chargeability images that are related to changes in the unsaturated zone that are of no interest here and can be disregarded.

## **DISCUSSION AND INTERPRETATION**

#### Geochemical analysis

For our experiment, the detailed analysis of Cahill et al. (2014) opens the unique opportunity to identify, which geochemical processes can be captured with the DC-IP field measurements. The main water sampling transect with 33 sampling locations coincides with the DC-IP profile, so that direct comparison is possible.

Cahill et al. (2014) show and analyze the detailed development of EC, pH, and dissolved element concentrations, in addition to undertaking comprehensive sediment characterization on core samples of varying depths. In their analysis, Cahill et al. (2014) find two dis-

Figure 6. Measured and computed IP decays for the preinjection (day 0) and injection (day 39) situation. The quadrupoles are the same as in Figure 2, and the baseline and time-lapse inversion results of Figures 4 and 5 were used to compute the forward responses (dashed lines). Observe how the day 39 response in panel (a) fits the measured data for small times ( $m_0$  controlled) but does not fit the tail of the curve. Changes in  $\tau$  and C would be necessary to fit the full curve.

tinct phases of chemical reactions: an advective elevated ion pulse and increasing persistent acidification. The images of EC and Al concentration in Figure 8 illustrate these two phases. The elevated ion pulse is the immediate reaction to CO<sub>2</sub> dissolving in the flowing groundwater, i.e., increases in aqueous concentrations of Ca (278 µM), Mg (579 µM), Na (1114 µM), Si (238 mM), and minor ions Ba (3.19  $\mu M)$  and Sr (2.05  $\mu M)$  — numbers in brackets are the maximum observed increases 1.5 m downstream of the injection (see Cahill et al. [2014] for details). Once dissolved, the CO<sub>2</sub> forms carbonic acid, which dissociates to release protons and HCO<sub>3</sub><sup>-</sup> ions; see Figure 9 for a sketch of the geochemical reactions that Cahill et al. (2014) identify. The increase in proton concentration (i.e., reduction in pH) induces geochemical processes, beginning with dissolution of reactive trace minerals followed by ion exchange/surface processes. The dissolved trace minerals were mainly aluminum hydroxides (Al(OH)<sub>3</sub>). Presumably, other minerals were dissolving in minor amounts, but direct effects were too small to be detected (see Cahill et al. [2014] for details). This increased ion pulse moves with the groundwater, and it is manifest as changes in EC (left panels in Figure 8). Consequently, EC is the clearest indicator for dissolved CO2 at Vrøgum.

Following the initial advective pulse behavior, water chemistry around the injection screens is observed to further evolve in what is described as a second phase of behavior characterized by increasing, persistent acidification. This secondary behavior was attributed to exhaustion of the sediments' buffering capacity (i.e., depletion of the most reactive trace minerals) allowing pH to decrease further and amphoteric/pH dependent trace elements (Al in particular) to be mobilized. Although the initial decrease in pH is clearly seen, Al concentrations (right panels in Figure 8) show more clearly the impacts of buffering exhaustion and acidification with significant releases into the groundwater observed in the final stages of the experiment. During buffering exhaustion, protons are consumed in the dissolution of reactive minerals present (specifically amorphous and crystalline forms of gibbsite), therefore resisting acidification and maintaining pH. However, once the minerals initially buffering the system have been exhausted, pH decreases further; a phenomena that is observed directly adjacent to the injection screens as described in the full geochemical study (Cahill et al., 2014).

Once the gibbsite-derived Al is mobilized, it moves advectively away from the area of increased acidification and likely precipitates, thereby ensuring that the Al anomaly remains highly localized. Following the injection phase, Al concentrations were observed to rebound with pH rebounding more slowly. This was attributed to exchanger-bound Al forming a store of acidity. As freshwater displaces the CO<sub>2</sub> charged groundwater, an amorphous gibbsitelike mineral is likely reprecipitated, and consequently stored acidity is released maintaining a low pH.

## Comparison of direct current-induced polarization results and geochemical measurements

Following the geochemical analysis, we use EC and Al as the primary indicators of the two main geochemical effects identified and expect the greatest level of correlation with DC-IP results. The DC-IP results were also compared with other dissolved element concentrations, but results were not conclusive. We use the water samples that were collected before the start of the injection (day -27) and on four days that agree with the timing of the inverted DC-IP data. The baseline sampling campaign used all 33 multilevel samplers, whereas



Figure 7. Resistivity  $\rho$  and normalized chargeability  $m_0/\rho$  time-lapse changes shown for days 39, 53, 77, and 114 after the beginning of the injection. The panels only show  $\rho$  and  $m_0/\rho$  for the area of interest (same region as in Figure 1c and black rectangle in Figure 5a), whereas the inversion used the full models and inverted for all four Cole-Cole parameters (as shown in Figure 5). The CO<sub>2</sub>-induced changes are visible as decrease in  $\rho$  and an increase in  $m_0/\rho$  close to the injection at x = 0.



Figure 8. Interpolated measurements of EC change and Al concentration from the groundwater sampling campaigns at days 36, 53, 79, and 113 after the beginning of the injection. Sampling locations are shown as black dots, if measurements exist for the specific sampling time, and as gray dots, if baseline measurements were used. The EC increases by ~50% when the advectively moving CO<sub>2</sub> arrives.



early sampling rounds after injection commencement focused around the injection well. Monitoring was extended along the flow line as the  $CO_2$  migrated downstream, using a 20% change in EC as a threshold to decide if a full sample should be collected.

For visualization and comparison with the DC-IP inversion results, the geochemical point measurements were interpolated by kriging (Figure 8). Kriging was performed using an exponential model with a range of 3.6 m that was fit to the experimental variogram. The interpolation area was restricted to the saturated aquifer, and areas without data are shown in gray. For a better comparison with the resistivity inversion results in Figure 7, ECs (left panels in Figure 8) are normalized by the baseline EC values (Figure 4b in Cahill et al., 2014) and shown as EC ratios. Assuming no significant surface conductivity and no change in the formation factor, the water EC ratios are inversely related to the resistivity ratios, and the color scales in Figures 7 and 8 are chosen to enable direct comparison. Al concentrations before commencement of the CO2 injection were very low and practically homogeneous (see Figure 7 in Cahill et al., 2014) and are therefore not shown. The average Al concentration was 2.3 µmol/l, the natural variation of background measurements at the same location  $\pm 1 \ \mu mol/l$ , and the standard deviation of all baseline measurements 1.5 µmol/l.

Comparing the left panels in Figures 7 and 8, one can observe that the DC/IP time-lapse inversions image the shallow low-resistivity (high-EC) feature in the correct size, location, and magnitude of change. The movement of the advective plume is also consistent between Figures 7e and 8e, and so is the slow rebound to baseline resistivity/EC around the injection wells after the end of the  $CO_2$ release. Although these main features are reliably recovered with the DC-IP inversions, some fine-scale features of the EC data and

EC increase below 10 m elevation cannot be resolved by the inversions. Geoelectric measurements have a large volume of subsurface sensitivity, which enables nonintrusive monitoring, but at the same time it limits the resolution (Ellis and Oldenburg, 1994). The resolution also decreases with depth, so that deeper features are more difficult to resolve. Additionally, shallow features can mask the deeper ones, which is the case here. The strong anomaly above the injection points and water saturation variations in the vadose zone create a strong signal that effectively masks the signal of the decrease in resistivity at depth. Nevertheless, the movement of the tracer at later times is correctly imaged at the depth, where it is sampled in the wells.

The changes in normalized chargeability  $m_0/\rho$  (right panels in Figure 7) show resemblance with Al concentrations in Figure 8. The correlation is not perfect, but the key feature, plume extent at different times agrees well. For example, the Al increase at day 79 extends a little further than x = 10 m, which is also the extent of the  $m_0/\rho$  anomaly. The source of the strong shallow increase in Al concentration is unknown, but except in the day 39 image, it also occurs in the normalized chargeability section. As for the resistivity, the normalized chargeability images are affected by resolution limitations, and they do not recover

some of the strong variability between neighboring water samples that are manifest of small-scale heterogeneity in groundwater chemistry. Due to the lower signal-to-noise ratio, chargeability parameters are actually poorer resolved than resistivities. The use of the Cole-Cole model also introduces further nonuniqueness by inverting for four parameter sets simultaneously. Due to the weak IP variations over time, only resistivity and chargeability changes could be reliably inverted. Strong changes of  $\tau$  and c can be excluded because they would have led to a higher data misfit, but small changes are likely to stay undetected in our inversions.

The causes for the increase in normalized chargeability are changes to the surfaces of the grains that are caused by the CO2-induced geochemical changes of the pore water. The measured decrease in chargeability that can be seen in the raw data (Figures 2 and 6) is in agreement with the laboratory analysis of Dafflon et al. (2013) that find a decreasing IP phase shift with a reduction in pH. Dafflon et al. (2013) also see a decrease of the IP effect in their field data that was collected in a CO2 injection experiment. The imaged increase in normalized chargeability, however, does not match with the findings of laboratory experiments of Lesmes and Frye (2001) and Skold et al. (2011) that find a decrease in quadrature conductivity with a decrease in pH. We therefore modeled the expected change in sediment surface charge in response to the geochemical reactions at our field site. A simple PHREEQC (Parkhust and Appelo, 2013) model using the most probable amounts of goethite (2.85 g/kg) and ferrihydrite (2.01 g/kg) in the sediment based on extractions on core material from the site was used to estimate the effect on the surface charge of the sediment on a lowering of the pH. For ferrihydrite, we use the PHREEQC standard database for hydrous ferric oxide and for goethite, the database used by Jessen et al. (2012). The measured



Figure 9. Injected gas phase  $CO_2$  dissolves into groundwater forming carbonic acid and dissociating, releasing protons and bicarbonate ions into solution. This acidification influences the IP signal by two mechanisms: (1) alteration of sediment particle surface charge and (2) dissolution of mineral grains (e.g., gibbsite) altering grain surfaces. These processes are linked to all other geochemical processes occurring, such as ion exchange and silica-proton interaction.

cation exchanger (Cahill et al., 2014) was also included, the effect being a buffering of the pH to values similar to the observed. In the batch model, exchanger and surfaces corresponding to the mentioned Fe-oxides were equilibrated with preinjection groundwater, and subsequently the system was equilibrated with a typically measured partial pressure of  $CO_2$  of 0.32, resulting in a drop in pH from 5.9 to 4.6 and an increase in the total charge on the Fe-oxide surfaces of 75%. This increase in surface charge could explain the increase in normalized chargeability that we see in our inversions. However, laboratory measurements on sediment cores from the Oksbøl field site would be needed to study the effect of geochemical changes on the IP effect in detail. A laboratory  $CO_2$ -injection experiment with DC-IP monitoring would be a great extension of this work, but it was unfortunately not part of the core project.

Overall, we find good agreement between the inverted decrease in resistivity and the directly measured increase in EC. However, not all anomalies in EC are imaged, mainly due to the resolution limitations of the method. The agreement between the inverted change in normalized chargeability and Al concentrations is somewhat weaker but still evident in our results. The geochemical modeling using PHREEQC confirms that an increase in normalized chargeability would be expected for the experiment at our field site. We see the main reason for the differences between the hydrological point measurements and our inversions in the resolution limitations. Acquiring data from the surface enables coverage of large areas, but it restricts the coverage of deep features. Installing electrodes in boreholes or otherwise below the groundwater table would greatly improve the detection reliability for slight changes in resistivity and chargeability. Unfortunately, such installations are costly and limit the lateral extent of measurements.

To our knowledge, this is the first study that images  $CO_2$ -induced variations in chargeability on the field scale, and thereby it demonstrates the feasibility of field-scale DC-IP monitoring and time-lapse full-decay inversion. DC-IP field instruments are currently being improved further and will enable even better measurement reliability and data quality in the near future. Development of 3D full-decay DC-IP inversion codes will also be available soon. Together, these instrument and code developments will allow much-improved monitoring of IP changes. Combined with laboratory experiments, this will enable monitoring of geochemical changes at a scale that is not feasible using water sampling in wells, and it could therefore play a major role in monitoring of  $CO_2$  from potential leaks.

Whether this monitoring method can be used for monitoring leakage of  $CO_2$  from pipes or borehole installations in large-scale  $CO_2$  underground storage projects is dependent on the ground water chemistry and the existing ions in the groundwater. Another consideration is the scale of a real monitoring setup, in which it will be physically difficult to cover much larger areas than a few hundred by a few hundred meters in 3D. In 2D, the lines can be of kilometer length, but in this case they have to be carefully located with respect to a potential leakage source to catch changes.

#### CONCLUSIONS

A controlled  $CO_2$  injection experiment featuring simultaneous recordings of high-quality DC resistivities, IP decays using surface electrodes and geochemical water sample data was conducted in a shallow sandy aquifer in western Denmark. The raw IP decays show a clear decrease in the IP effect in response to the  $CO_2$  injection, especially for configurations sensing changes in the shallow subsurface around the injection wells. After cessation of the  $CO_2$  injection, decays rebound slowly to their preinjection values, thereby demonstrating the long-term stability and reliability of field-scale IP measurements.

This study is the first to invert the full IP decay curves and DC measurements for a time-lapse data set. Time-lapse variations are small, and it is therefore crucial to adapt the processing and inversion settings to target small changes. Various data processing schemes, error estimation, and inversion methods were tested to obtain best results. The final DC-IP time-lapse inversions illustrate that resistivity decreases, whereas normalized chargeability increases in reaction to the injected CO2. The features of change in resistivity and normalized chargeability are different in shape and evolve differently over time. Comparison with the geochemical data indicates that resistivity and normalized chargeability image two different geochemical processes. Change in resistivity represents the advectively moving high-EC plume that forms resulting from dissolution of injected CO2 in the pore water. Changes in normalized chargeability are related to increasing and persistent acidification, seen as an increase in Al concentration in the water samples, that alters the electric charge density on the grain surfaces.

These results demonstrate that field-scale DC and IP data can image geochemical subsurface processes and actually discriminate between different processes in the pore water and on the grain surfaces. With recent developments in instrumentation and inversion software, full-decay time-domain DC-IP monitoring can now play a more important role in geochemical studies, especially when paired with laboratory measurements.

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