Inverting self-potential data for redox potentials of contaminant plumes

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Abstract

We present the first inversion method that uses self-potential data to invert for the redox potentials of contaminant plumes. A two-layered electrical conductivity structure, in which the boundary corresponds to the water table, is considered. Furthermore, the electrical-dipole sources are assumed to be vertical and located at the water table. The inverse method is applied to surface self-potential measurements made in the vicinity of the Entressen landfill (southern France). The estimated redox potentials correlate well with *in situ* measurements and their amplitudes are retrieved satisfactorily. This is the first method (to our knowledge) that can be used to estimate the redox potential of contaminant plumes non-invasively and remotely without any *in situ* measurements.

1. Introduction

The self-potential (SP) method is a passive geophysical method, in which the electrical potential distribution is mapped using a set of non-polarizing electrodes. The recorded signals are affected by anthropogenic noise—mainly 50/60 Hz and harmonics—and telluric currents [*Perrier et al.*, 1997]. If these sources of noise can be removed or if they are small, two major contributions to the collected SP signals remain in the case of contaminant plumes enriched in organic matter. The first contribution is related to pore water flow in the saturated and unsaturated zones (i.e., the streaming potential contribution) [e.g., *Sill*, 1983; *Linde et al.*, 2007a, 2007b], whereas the second is related to redox processes associated with contaminant plumes [e.g., *Naudet et al.*, 2003, 2004; *Arora et al.*, 2007]. For this latter case, the electromotive force that drives the current is the gradient of the redox potential in the conductive medium.

The self-potential method is a promising tool for remote and non-intrusive monitoring of organic-rich contaminant plumes. *Naudet et al.* [2003, 2004] reported a correlation coefficient of 0.85 between *in situ* redox potential measurements made at the Entressen municipal landfill in southern France and residual SP that had been corrected for streaming potentials. *Naudet et al.* [2005] stimulated sulfato-reducing bacteria with organic nutrients in a sandbox experiment and found a correlation coefficient of 0.85 between self-potential signals and redox potentials following the stimulation. *Arora et al.* [2007] proposed a geobattery model associated with microbial breakdown of contaminants at the plume boundaries. This battery is hypothesized to exist as (1) the plume boundary is associated with a strong redox gradient between highly reducing conditions within the plume (due to biodegradation and oxygen depletion) and oxidized zones outside of the plume, and (2) microbial biofilms and precipitation of metallic particles that can provide an electron conductor to complete the circuit required for the geobattery. Field data as well as numerical modeling indicated that the redox contribution can be explained by dipoles distributed throughout the water table with a strength that is proportional to the difference in the redox potentials between the aquifer and the vadose zone.

Here, we present the first inversion method that inverts residual self-potential data to estimate the redox potential distribution in contaminant plumes. The resulting models provide a fast and non-intrusive means to identify the location of organic-rich pollution plumes and they can be used to identify the most heavily contaminated regions. Such models could be useful to determine where to drill boreholes and collect geochemical data. Of course, inversion of potential fields, such as self-potential, are inherently non-unique. Uniqueness can be imposed in different ways, for example, by searching for source distributions that are spatially compact [*Minsley et al.*, 2007]. We assume that the source signals are associated with the water table because of rapid bacterial growth in the nutrient and oxygen-rich environment surrounding the water table. A similar situation occurs at the end-boundaries of the plume but the gradient of the redox potential is expected to be smaller because of the lower amount of available oxygen in the saturated zone compared with the vadose zone. Based on these assumptions, we decided to constrain the model space by defining interfaces where current sources might be located (i.e., the water table) and by favouring models with a flat distribution of the current source density. We invert the residual SP estimates from Entressen [*Naudet et al.,* 2003, 2004; *Arora et al.*, 2007] to estimate the distribution of redox potentials within the saturated zone. We assume that the current sources are located in the vicinity of the water table and that the electrical conductivity distribution is adequately approximated by the two horizontal layers identified in *Naudet et al.*'s [2004] electrical resistivity tomograms. These assumptions allow us to use fast quasi-analytical solutions based on the mirror image method to solve the forward problem. In contrast to previous work [e.g., *Naudet et al.*, 2003, 2004; *Arora et al.*, 2007], no *in situ* measurements of redox potentials are necessary to reconstruct the subsurface redox conditions.

2. The forward problem

The SP distribution is given by the solution to the following Poisson equation

$$\nabla \cdot \sigma \nabla \varphi = \nabla \cdot \left(\mathbf{j_{sc}} + \mathbf{j_{rc}} \right), \tag{1}$$

where σ is the electrical conductivity of the ground (S m^{-1}), φ is the SP signal (V), $\mathbf{j_{sc}}$ is the streaming current density (A m^{-2}), and $\mathbf{j_{rc}}$ is the current density associated with redox processes (A m^{-2}). We define the residual SP φ_{res} as the difference between the measured SP φ and the estimated streaming potential φ_{sc}.

Linde et al. [2007a] derived an expression for $\mathbf{j_{sc}}$ that is valid under both saturated and unsaturated conditions

$$\mathbf{j_{sc}} = Q_{\mathrm{v,sat}} \phi \mathbf{v}, \tag{2}$$

where $Q_{\mathrm{v,sat}}$ is the excess charge density in the pore space under saturated conditions (C m^{-3}), ϕ is the porosity, and $\mathbf{v}$ is the average pore water velocity (m s^{-1}). An accurate estimate of $\mathbf{j_{sc}}$ can only be obtained with a high-resolution hydrological model that provides $\mathbf{v}$ under both saturated and unsaturated conditions, see Linde et al. [2007a] for details. When no hydrological model is available, it is necessary to rely on simplified models to obtain $\nabla \cdot \mathbf{j_{sc}}$ (i.e., the source term that is responsible for the streaming potential). In this work, we removed the streaming potential contribution using a Bayesian method based on piezometric data and empirical relationships between the self-potential signal measured outside the contaminant plume and the water-table depth [*Arora et al.*, 2007; *Linde et al.*, 2007b].

The residual SP signal φ_{res} is then given by the solution of

$$\nabla \cdot \sigma \nabla \varphi_{res} = \nabla \cdot \mathbf{j_{rc}} \tag{3}$$

using appropriate boundary conditions. The work of *Arora et al.* [2007] suggests that the source of the redox driving currents coincides with the water table, where microorganisms have access to both oxygen and nutrients. Oxidation is assumed to take place just below the water table, whereas reduction is assumed to take place just above it. Electron transfer is assumed to occur through "microbial nanowires" [*Reguera et al.*, 2005]. We further assume that the water table is parallel to the ground surface, which is only slightly inclined, and that the gradients of the redox potential at the other plume boundaries are negligeable because of the low amount of available oxygen in the saturated zone. Accordingly, the gradient of the redox potential is practically vertical. In addition, we assume that the electrical conductivity distribution is known from geolectrical surveys and that it can be approximated by two horizontal layers with an interface at depth *d*. These assumptions allows us to formulate a linear inverse problem in which estimates of φ_{res} can be used to infer the redox conditions within a contaminant plume relative the redox conditions in the surroundings.

3. The inverse problem

The data vector **d** consists of the residual electrical potential φ_{res} at each of the *N* SP stations, with respect to a reference electrode that is located in an uncontaminated upstream area. The model vector **m** consists of *M* pairs of uniform current source densities that are distributed over rectangular portions of the water table. Each pair of current source densities are thought to consist of a current source that is associated with oxidation at a distance *h*/2 below the water table and a current sink of equal magnitude that is associated with reduction at a distance *h*/2 above the water table. The effective separation between oxidation and reduction *h* can be arbitrarily chosen as long as it is much smaller than the depth to the water table. Since the self-potential method can only resolve electrical dipole moments, we keep *h* fixed and invert for the current source densities. The linear forward model is given by

$$\mathbf{d} = \mathbf{F}\mathbf{m}, \tag{4}$$

where column *m* of the forward kernel **F** corresponds to the contribution to **d** from the *m*th discretized portion of the water table. To a first order, the *m*th pair of uniform current source densities can be approximated by solving Equation 3 for unit current injections and by multiplying the resulting electrical potential with the area of the *m*th discretized portion of the water table. This approximation is valid when the model discretization is small compared to the distance of the discretized area to the SP stations located at the surface of the ground. To decrease the size of *M* in order to decrease the size of the inverse problem and still allow accurate forward calculations, we discretize the area that corresponds to each model parameter *m* into $k \times k$ subdomains and sum the contributions from all subdomains to obtain the total contribution from model parameter *m*. It is prohibitively expensive to use finite-element models to calculate **F** for arbitrary electrical conductivity models for study areas that are much larger than the depths to the current sources. In the field example considered in Section 4, a finite-element mesh would consist of approximately 10^9 nodes when using a structured grid. Even if the number of nodes could be reduced by using an unstructured grid [e.g., *Rücker et al.*, 2006], the calculation of **F** would still be very time-consuming. In this work, the conductivity model is restricted to two horizontal layers (i.e., the upper one represents the vadose zone and the lower one represents the saturated zone) for which quasi-analytical and fast solutions can be obtained using the mirror image method [e.g., *Zhdanov and Keller*, 1994]. The mirror image method is based on an analogy with optics where an infinite series of reflections and transmissions at layer boundaries are used to calculate the resulting electrical potentials from point current injections in a layered media. A conductivity model that consists of only two layers is simple, but it is a reasonable first-order assumption for study areas that are fairly one-dimensional.

The data errors are assumed to be normally distributed and independent, which makes the data covariance matrix $\mathbf{C}_d$ diagonal. The iterative LSQR method [*Paige and Saunders*, 1982] is used to solve the following linear inverse problem in a least-squares sense

$$\begin{bmatrix} \mathbf{C}_{\mathbf{d}}^{-0.5}\mathbf{F} \\ \lambda \mathbf{W}_{\mathbf{m}}^{-0.5} \end{bmatrix} [\mathbf{m}] = \begin{bmatrix} \mathbf{C}_{\mathbf{d}}^{-0.5}\mathbf{d} \\ \mathbf{0} \end{bmatrix}, \tag{5}$$

where $\mathbf{W}_{\mathbf{m}}^{-0.5}$ is a regularization term and λ is a trade-off parameter between regularization and data fit. We perform the inversions using a flatness regularization term that penalizes horizontal gradients of the current source densities. The LSQR algorithm terminates when a model with a weighted RMS of one has been found. If the target misfit is not reached after a predefined number of conjugate gradient steps, λ is successively decreased until the target misfit is reached.

Arora et al. [2007] postulated the following relationship between current source density and redox conditions

$$\mathbf{j}_{\mathbf{rc}} = -\sigma \nabla E_h, \tag{6}$$

where E_h is the redox potential (V). Using Equation (6), we can calculate the corresponding redox potentials in the saturated zone $E_{\mathrm{h},2}^{m}$ based on the estimated current densities m from

$$E_{\mathrm{h},2}^{m} = -\frac{hm}{\sigma_H} + E_{\mathrm{h},1}^{m}, \tag{7}$$

where σ_H is the harmonic mean of the electrical conductivities of the two layers and $E_{\mathrm{h},1}^{m}$ is the redox potential in the unsaturated zone. The estimated source current densities m are not meaningful by themselves since they are inversely related to the arbitrarily chosen value of h, but the electrical dipole moment hm appearing in Equation 7 is well-defined. Equation 6 indicates that we can only resolve differences in redox potentials when inverting residual SP data and that we must assign values to $E_{\mathrm{h},1}^{m}$ in order to estimate $E_{\mathrm{h},2}^{m}$.

Electrical conductivity models are generally poorly known for study areas that cover several km^2 and it is therefore important to assess the sensitivity to erroneous electrical conductivity models. We have calculated the sensitivity of the mean difference in inverted redox potential $E_h^{mean} = \sum_{m=1}^{M} \frac{E_{h,1}^m - E_{h,2}^m}{M}$ with respect to changes in σ_1 (Figure 1a), σ_2 (Figure 1b), and the thickness of the vadose zone d (Figure 1c), for a reference model of σ_1=0.01 S m^{-1}, σ_2=0.01 S m^{-1}, and d=3. For this reference model, the inverted redox potential is overestimated by 36% if the electrical conductivity in the top layer is overestimated by a factor of ten and it is underestimated with 3% if the electrical conductivity is underestimated by a factor of ten. The opposite is true for the underlying half-space. The sensitivity to the thickness of the top layer is approximately linear with a 1.3% overestimation in E_h^{mean} if the depth is overestimated by one meter. It appears that an order of magnitude estimate of the electrical conductivity structure is sufficient to obtain relevant estimates of contaminant-plumes' redox potentials.

4. The Entressen field example

The Entressen landfill is one of Europe's largest open landfills. It is located close to Marseille, France (see *Naudet et al.* [2004] for details). To perform the inversion (see Equation 5), we used *Arora et al.*'s [2007] residual SP estimates displayed in Figure 2a, in which the streaming potential contribution was computed using the Bayesian method outlined by *Linde et al.* [2007b]. The electrical conductivity model was assumed to consist of two horizontal layers with electrical resistivities of 1000 Ohm-m in the upper unsaturated three meters and 100 Ohm-m in the underlying saturated half-space (see *Naudet et al.* [2004] for two-dimensional electrical resistivity models). It is further assumed that both the topography and the water table are horizontal; the slope of the water table at Entressen is 5 per mil. The residual SP data was assigned a uniform standard deviation of 20 mV [*Naudet et al.*, 2004]. The inversion was carried out with a model discretization of 30 × 30 m^2 to get a resolution that is roughly comparable to the station spacing of 10-20 m, k was 60 corresponding to a 0.5 × 0.5 m^2 discretization of the forward problem that allowed us to solve Equation 3 assuming a unit current injection, and h was arbitrarily chosen as 0.06 m. A model with a weighted RMS of 1 was obtained with λ=750. A scatter plot between the simulated SP and the residual SP estimated from the measured SP data is shown in Figure 2b. The model does not reproduce all data equally well, since the uniform regularization makes it difficult to fit large negative values that are confined to small areas. A map of redox potentials in the saturated zone was constructed from Equation 7 and by assuming that $E_{\mathrm{h},1}^{m}$ had a constant value of 114 mV (Figure 2c), which is the measured value at the uncontaminated reference station. The model has an appearance similar to the interpolated residual SP data (see Figure 2a), but it is smoother and the anomalies are more confined to the vicinity of the SP profiles. Note that the model is only reliable in the vicinity of the measurement points and that its values at unsampled points are strongly affected by the regularization operator used (see Equation 5). Finally, a scatter plot between *in situ* redox potentials and collocated inverted estimates of redox potentials are shown in Figure 2d. The correlation coefficient between the measured and inverted redox potentials is 0.93, which is similar to the correlation coefficient of 0.92 between residual SP data and available redox measurements (see *Arora et al.*, [2007]). This correspondence was expected, since the developed inverse problem is linear and we assumed a layered electrical conductivity structure. The magnitude of the estimated redox potentials correspond well with the *in situ* measurements. The inverted magnitudes in the contaminated areas are slightly underestimated because of the regularized character of the resulting models.

5. Concluding remarks

Bacteria-mediated redox processes are thought to behave like geobatteries, in which a current is created between the reducing and oxidizing part of the system [*Naudet and Revil*, 2005]. This makes surface self-potential measurements sensitive to redox processes occuring in shallow unconfined aquifers. Empirical relationships between residual SP estimates and redox conditions are limited, because *in situ* measurements are necessary and the validity of empirical relationships at unsampled locations are uncertain. We have developed the first inversion method that estimates the redox conditions of contaminant plumes from residual SP data. Residual SP estimates from the Entressen landfill in southern France were inverted and the predicted redox potentials correlated well with *in situ* measurements (the correlation coefficient is 0.93) and the predicted magnitudes were only slightly lower than those measured *in situ*. Since *in situ* redox measurements are problematic and error prone (Christensen et al., 2000), our results suggest that SP data might under favourable conditions provide estimates with a comparable accuracy. The inversion method presented here could be extended to arbitrary electrical conductivity distributions by replacing the calculation of the forward kernel with finite element or finite difference computations.

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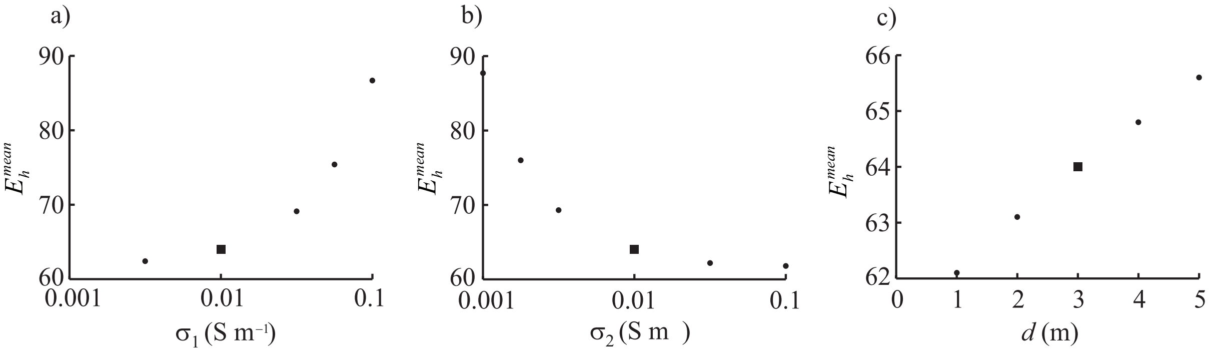

Figure 1: The sensitivity of the mean difference in the inverted redox potential E_h^{mean} is evaluated with regard to errors in (a) the electrical conductivity in the vadose zone σ_1, (b) the electrical conductivity of the aquifer σ_2, and (c) the depth to the water table d where the reference model is indicated by the filled rectangles.

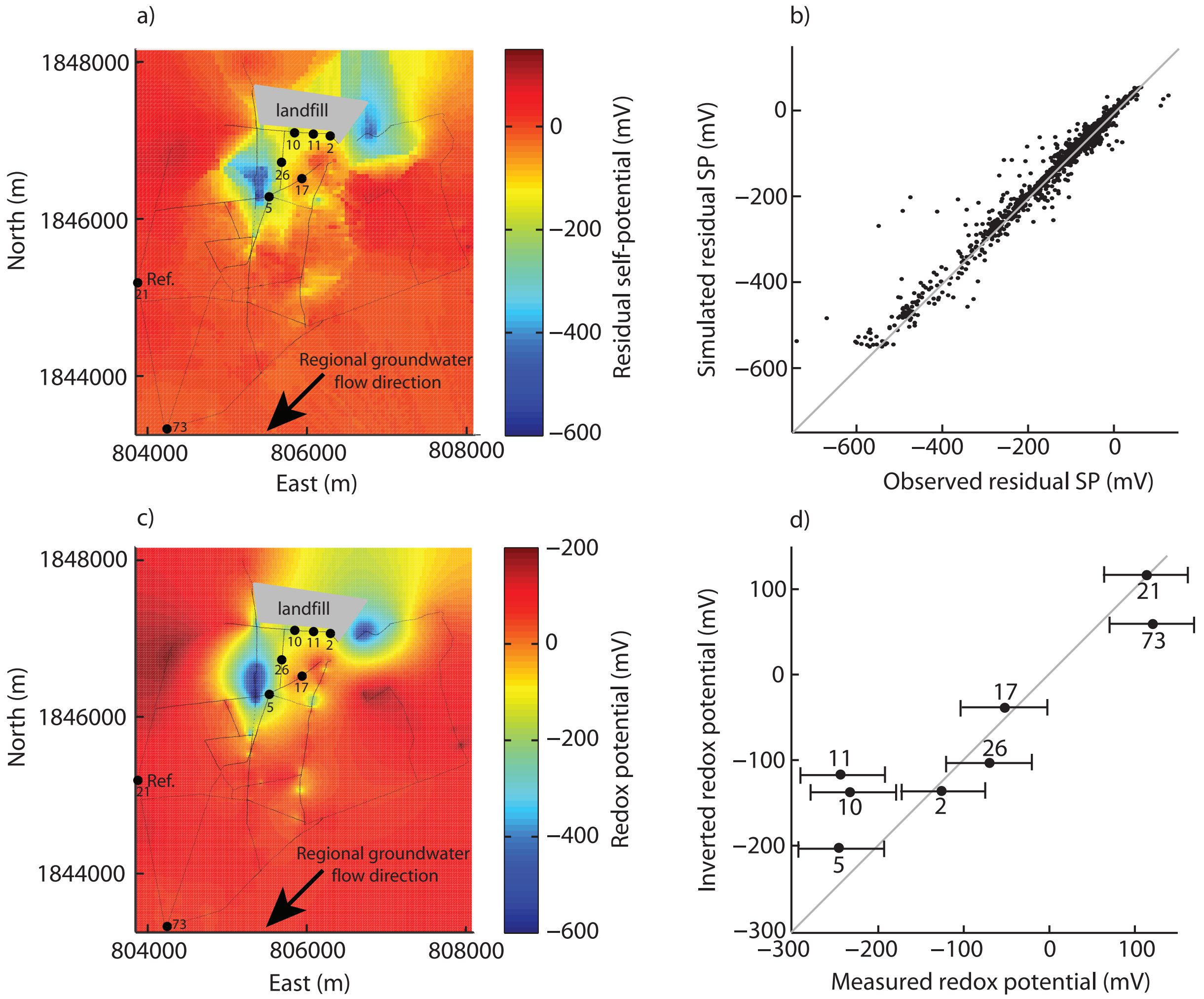

Figure 2: (a) Residual SP map at the Entressen landfill (adapted from *Arora et al*., [2007]), in which the black lines indicate the SP profiles (2417 SP measurements). (b) Comparison of simulated SP with the residual SP estimated from the measured SP data. The response of the inverted model fits the residual SP to the estimated standard deviation of 20 mV reported by *Naudet et al.* [2004]. (c) Inverted redox potential in the aquifer at Entressen. (d) Comparison of inverted redox potentials in the aquifer with *in situ* measurements from Entressen reported by *Naudet et al*. [2004] (the correlation coefficient is 0.93).