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Relationship between self-potential (SP) signals and redox conditions in contaminated groundwater

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[1] In situ measurements of redox potential are rather difficult to perform and provide only sparse information on its spatial distribution. To delineate redox fronts in a contaminant plume, the self-potential (SP) method can be a helpful complement to geochemical measurements. Here, we apply the SP method to the Entressen municipal waste landfill (south-eastern France) over a 20 km^2 area. The results show a large negative SP-anomaly of ~ -400 mV with respect to a reference station taken outside the contaminant plume. Once removed the electrokinetic component associated with groundwater flow, the residual self-potential signals are linearly correlated with in situ measurements of redox potential. We propose a quantitative relationship between self-potential and redox potential, which would be used to invert self-potential measurements in terms of in situ redox potential values in contaminant plumes. *INDEX TERMS:* 5109 Physical Properties of Rocks: Magnetic and electrical properties; 5139 Physical Properties of Rocks: Transport properties; 1832 Hydrology: Groundwater transport; 4851 Oceanography: Biological and Chemical: Oxidation/reduction reactions; 1831 Hydrology: Groundwater quality. **Citation:** Naudet, V., A. Revil, J.-Y. Bottero, and P. Bégassat, Relationship between self-potential (SP) signals and redox conditions in contaminated groundwater, *Geophys. Res. Lett.*, *30*(21), 2091, doi:10.1029/2003GL018096, 2003.

1. Introduction

[2] The knowledge of redox potential is crucial in understanding the evolution of contaminant plumes. However, direct measurements of this parameter in the field are difficult. To get accurate redox values, many constraining precautions must be taken, like avoiding the entrance of O_2 into the sampling cell. These measurements are time-consuming because quasi-equilibrium conditions must be reached in order to obtain truly representative values (*Christensen et al.* [2001]). In addition, the determination of the spatial distribution of the leachate properties requires a large number of sampling wells. Consequently, it is not surprising that very few representative maps of the redox potential distribution have been established to date.

[3] It follows that a geophysical method sensitive to the redox potential distribution into the contaminated aquifer would be particularly welcome. The self-potential method, based on passive measurement of the natural electrical potential at the ground surface, offers such a possibility. Several field studies carried out over waste dumps show negative SP values in comparison with a reference electrode located in an undisturbed area (*Weigel* [1989], *Hämmann et al.* [1997], *Vichabian et al.* [1999], *Nyquist and Corry* [2002]). These electrical anomalies could be the signature of oxido-reduction phenomena occuring at depth in the contaminated groundwater. Here, we present the results of a SP survey downstream of the Entressen landfill (south-eastern France). A large negative SP-anomaly is detected near the redox front. The minimum value (~ -400 mV) is located near the settling basins. A comparison with the available geochemical data suggests that this SP anomaly can be attributed to high redox potential gradients in this area.

2. The SP Method

[4] The self-potential signals are naturally occurring electric field measured at the ground surface with non-polarisable electrodes. The origin of SP has two main components: (1) the electrokinetic contribution associated with groundwater flow through the permeable soil and (2) oxido-reduction phenomena. The underlying physics of electrokinetic phenomena is fairly well established. SP-signals and hydraulic head gradients are correlated through an electrokinetic coupling coefficient, which ranges from -10 mV/m to -1 mV/m of hydraulic head (e.g., *Revil et al.* [2003]). However, no theoretical model has been established to tie the strength of SP-signals to redox potential gradients, except for ore deposits sites (e.g., *Bigalke and Grabner* [1997]). *Timm and Möller* [2001] show that redox potential gradients are the source of negative SP-anomalies with respect to a reference electrode taken in an undisturbed area.

3. Presentation of the Site and Field Survey

[5] The Entressen landfill (Figure 1a) is the biggest open-air landfill in Europe with about 600,000 tons per year of municipal and domestic wastes stored since 1912. The landfill extends over $\sim$0.5 km^2 and reaches a height of 30 meters. Landfill leachates percolate to a shallow unconfined aquifer (1–8 meters depth) formed by the old alluvial plain of the Durance river. The portion of the aquifer impacted by the landfill is composed of quaternary alluviums, including calcareous, metamorphic, and endogenous stones. The hydraulic conductivity is high ($K = 8.5\ 10^{-3}$ m/s), except for

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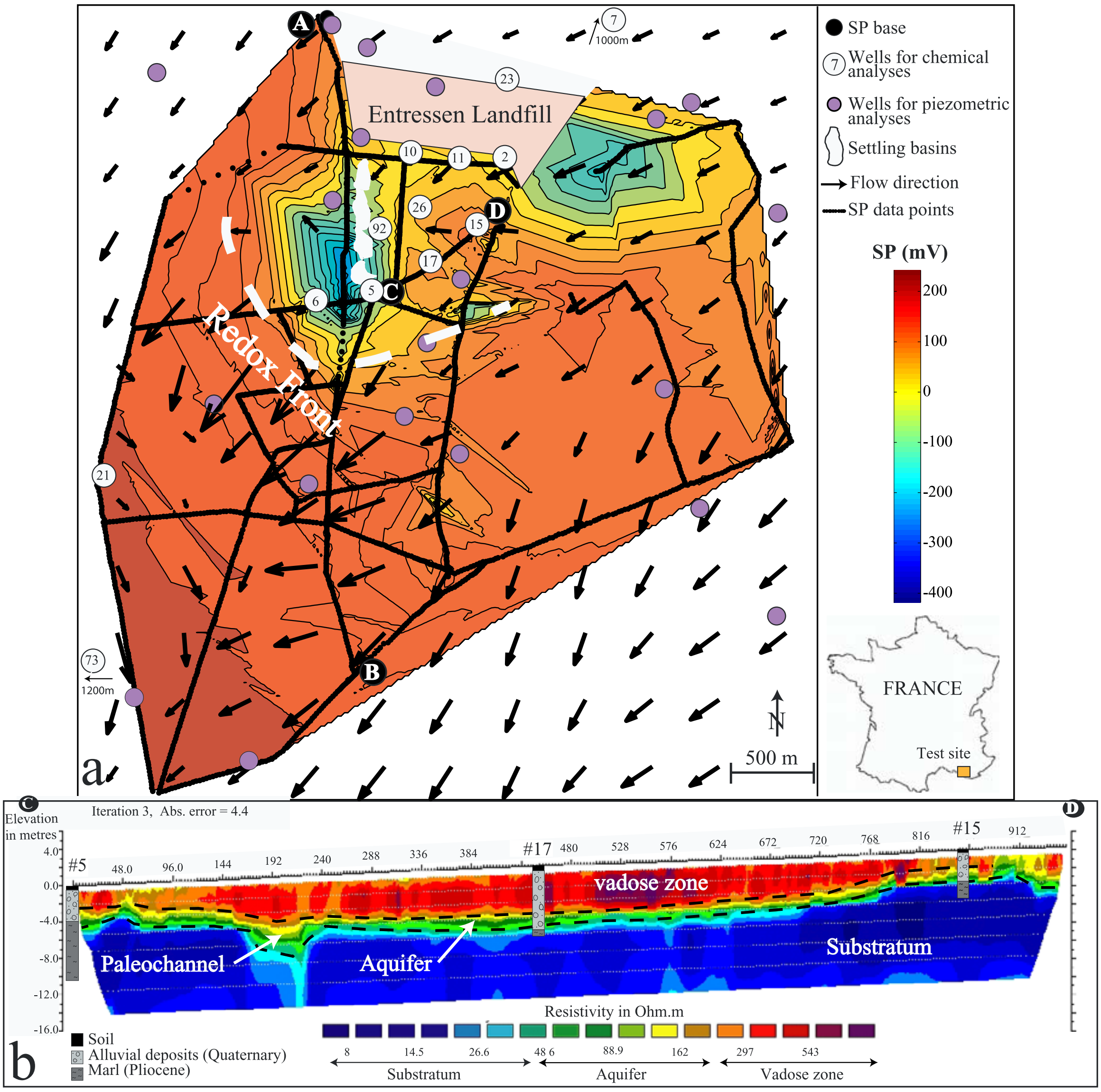

Figure 1. (a). Self-potential map obtained from a linear interpolation of over 2800 SP measurements (black dots). The electrode spacing is 10 m in the first two kilometers from the landfill and 20 m elsewhere. Numbered open-circles correspond to the piezometers where geochemical analyses are available. Arrows indicate the groundwater flow directions determined from about thirty piezometric head data. (b). Electrical Resistivity Tomography (ERT) with a Wenner-α configuration (profile CD, 1a). The unit electrode spacing is 3 meters. Note the presence of paleochannels of the Durance river.

the East side of the landfill where $K \approx 10^{-6}$ m/s because the presence of a clay-rich lens, which reaches the ground-surface. The thickness of the impermeable substratum is >20 m and composed of marls of Pliocene age (*Colomb and Roux* [1978]). As a preliminary step, we performed an electrical resistivity tomography (ERT) using the ABEM multi-electrode equipment. The profile shown in Figure 1b, constrained by data from 3 boreholes, reveals the shallow aquifer underlying the marly substratum. The overall groundwater flow direction is NE-SW but a few high transmissivity paleochannels locally modify the flow direction (Figure 1b). The hydraulic gradient is 3‰ and the water level change over the year is around one meter (*Vilomet et al.* [2001]). Few piezometers are available for groundwater quality information (Figure 1a). The methodology and results of the geochemical sampling and measurements performed between 1998 and 2000 were discussed in *Vilomet et al.* [2001]. Their study shows that the contaminant plume extends to a maximum of 4.6 km away from the landfill (down to well #73) with an anaerobic zone located in the two first kilometers (down to well #6). Chemical analyses and redox potential are there available for comparison with the SP measurements.

[6] From September 2001 to March 2002, we carried out a SP survey using a high-impedance voltmeter (100 MΩ), insulated single-conductor wire (500 m) and 2 non-polarisable Pb/$PbCl_2$ Petiau electrodes. We used a combination of the fixed-base and the gradient configuration techniques to reduce the influence of electro-telluric variations and cumulative errors (see *Perrier and Morat* [2000]). One

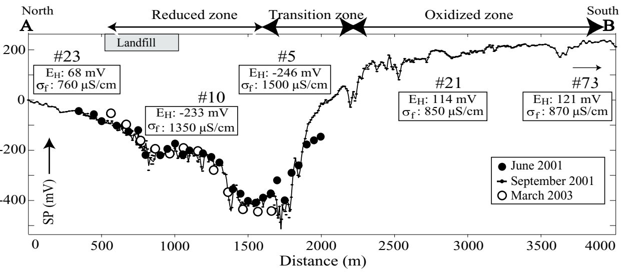

Figure 2. North-South SP-profile located on Figure 1a. Electric conductivity of the ground water (σ_f) and redox potential (E_H) measured into wells #23, #10, #5, #21 and #73 correlate with the SP anomaly. Also note the good stability of the SP signals over time.

electrode was the stationary base electrode while the other was moved to each measurement station in order to scan the electrical potential at the ground surface. The base station is changed all the 500 m. To improve electrical contact between the ground and the electrode at each station, including the base station, small holes were dug and filled with a salty bentonite mud. Additional diffusion potentials can occur at electrodes set up in this way, but their influence vanishes when measurements are made between two electrodes in contact with the ground in the same way. To reduce cumulative errors, survey lines were designed to form a web with numerous tie-in points. Tie-in loop closure errors were distributed among all the readings around each loop. The data reproducibility was better than 10 mV and the signal was very stable during the year as shown by repeating the survey along the same profile (Figure 2).

4. Results and Discussion

[7] Note a general increase of the SP signals along the groundwater flow direction in Figure 1a, corresponding to the electrokinetic conversion of the hydraulic head. In the South part of this field, geochemical analyses and redox values indicate an aerobic area with no contamination (wells #21 and #73, Table 1). In this area, we find an excellent correlation between the self-potential φ (in mV) and the piezometric head difference ($h - h_0$) (in m) with h_0 the piezometric head level at the SP base station. Such

Table 1. Chemical Analyses Realized by the City of Marseille (11/2001) and by *Vilomet et al.* [2001] for the Piezometer #6 and the Dissolved O_2 Concentration % of Saturation (01/2000)

Wells	E_H (mV)	σ_f (µS/cm)	SO_4^{2-} (ppm)	Cl^- (ppm)	NH_4^+ (ppm)	O_2 (%)
2	−126	7400	280	765	960	1.63
5	−246	1500	160	110	1.3	–
6	–	1520	200	110	–	4.5
7	138	670	100	24	0.1	63.8
10	−233	1350	120	105	46	4.9
11	−244	3700	180	425	185	1.96
15	−237	5500	140	920	250	1.35
17	−52	910	140	61	3	–
21	114	850	120	48	0.3	9.76
23	68	760	110	25	0.2	–
26	−70	2300	270	235	55	–
73	121	870	130	51	0.1	50
92	−63	1150	160	100	63	–

a correlation results from the electrokinetic contribution to self-potential. Based on the first-order linear relationship determined by *Revil et al.* [2003], the analyse of the data located in the South part of the studied site yields $\varphi = -10.60(h - h_0) + 56.10$. This equation is used to remove the electrokinetic contribution to the SP-signals measured on the site.

[8] The first two kilometers downstream the landfill are strongly anaerobic. The concentration of dissolved electron acceptors (O_2, SO_4^{2-}) and the redox potential are reduced in this area (wells #2, #10, #11, #15, #17, #92, Table 1). In this region, the SP signal displays a strong negative anomaly of ~ -400 mV close to the settling basins. This prominent SP anomaly can be attributed to a basin leak and/or the presence of a redox front. Figure 2 shows a North-South profile across the zone where geochemical changes are observed. The SP-signal decreases progressively in the anaerobic zone, then drastically increases through the redox front, and finally reaches normal background values in the more oxidized zone. Along this profile, the negative SP anomaly is therefore well correlated with the redox potential in the contaminant plume. On Figure 3b, we plot the redox potential versus self-potential residuals obtained by removing the electrokinetic contribution to the SP. The data from wells #7, #26, and #92 were rejected because they did not have corresponding SP measurement but interpolated SP value. Since well #15 is above the clay lens and shows unusual variations during the year, this point is not considered for calculating the correlation. We obtain a reasonable correlation ($R^2 = 0.85$) between the residual self-potential

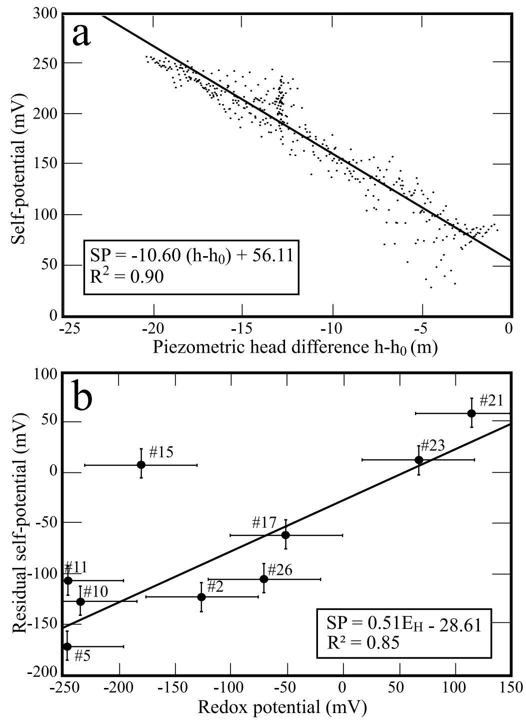

Figure 3. (a). Self-potential signals (in mV) versus hydraulic head variations in the South part of the studied zone and with h_0 taken at the SP base station. (b). Redox potential measured with an error of ±50 mV (Table 1) versus the residual self-potential estimated with an error of ±20 mV.

(i.e., corrected from the electrokinetic effect) and redox potential measurements with a slope of 0.51 ± 0.09. Without removing the electrokinetic component to the SP-values the correlation was $R^2 = 0.61$.

[9] The thermodynamic source of the SP signals corresponds to a gradient of redox potential. The transfer of charges between the different redox zones would be provided either by diffusion of ionic species and/or migration of electron through biofilms of bacteria. Indeed, micro-organisms derive energy from redox reactions to maintain life-sustaining processes (*Christensen et al.* [2001]), and when local conditions are favourable (oxygen and organic-comtaminants), they develop as biofilms through the connected porosity (*Vayenas et al.* [2002]). Recent researches on micro-organisms of marine sediments realized both in the laboratory (*Bond et al.* [2002], *Tender et al.* [2002]) and in the field (*Delong* [2002]) demonstrated that electricity can be produced from marine sediments owing to bacterial activity.

[10] From these considerations, we propose a formulation derived from the hydroelectric phenomena (*Revil et al.* [2003]). Assuming that the redox potential E_H (in V) is analogous to the hydraulic charge h in electrokinetic phenomena, the total current density $\mathbf{j}$ (in A m^{-2}) is given by $\mathbf{j} = \sigma\mathbf{E} + \mathbf{j}_s$, where σ is the electrical conductivity of the porous rock (S m^{-1}), $\mathbf{E} = -\nabla\varphi$ the electrical field (in V m^{-1}), φ the self-potential associated to redox effect (in V), $\mathbf{j}_s$ (in A m^{-2}) the source current density $\mathbf{j}_s = \sigma\nabla(C_H E_H)$, and C_H a dimensionless sensitivity coefficient relating the resulting electrical potential variation to the redox potential difference E_H. This coefficient can be obtained from the field data by correlating the in situ redox potential measurements to the local value of SP. From Figure 3b, $C_H \equiv (\partial\varphi/\partial E_H)_{\mathbf{j}=0} = 0.51 \pm 0.09$.

5. Concluding Statements

[11] The present study suggests that organic-rich contaminated plumes behave like geobatteries. These geobatteries are a source of an electrical field, which signature can be recorded at the ground surface as self-potential signals. A reasonable correlation was obtained between self-potential corrected from the electrokinetic effect and redox variations. Additional research works need to be carried out to understand the role of the biofilms and the physics of this phenomenon. Then, with a model of such geobattery, inverse problem algorithms will be used to constrain the redox potential distribution of the contaminant plume from SP measurements performed at the ground surface.

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