

# Spontaneous potential as a method for mapping degrading organic contaminants: an explanation of its variable efficacy

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## Summary

Spontaneous potentials (SP) are natural electrical potentials in the earth and in the past decade they have been used to delineate groundwater organic contaminant plumes. The method is attractive because of the simplicity of the equipment necessary and the rapidity at which the non-intrusive measurements can be made.

We have carried out SP surveys at two hydrocarbon impacted sites in Alberta where we failed to see the expected signal, and propose that the strength of the SP signal from degrading organic pollutants is dependent on reaction rates. To support this hypothesis we are creating a numerical model for degradation in which we will be able to vary reaction rates and compare the SP signatures generated.

## Introduction

Spontaneous potentials are generated by electrokinetic, electrochemical and thermoelectric mechanisms, and can be measured using two liquid junction electrodes and a voltmeter. When mapping contaminant plumes the electrochemical component of SP is of interest as it is thought that the redox gradients in the degradation halo generate measurable electrical gradients. Examples of anomalies include: -600 mV over a jet fuel plume (Shi, 1998), -80 mV over tomato canning waste (Nyquist and Corry, 2002) and -400 mV over landfill leachate (Naudet et al., 2003).

We performed two SP surveys at hydrocarbon impacted sites in Alberta to better understand the mechanisms and test the applicability of this method locally. Neither site showed the expected negative anomaly, even after correction for anthropogenic noise.

## Theory and Method

The current theoretical model follows from models developed for electrochemical SP anomalies over ore deposits and it links SP with redox potential (Eh) by assuming something equivalent to electronic conduction, perhaps through microbial mats (Revil et al., 2009).

$$\nabla \cdot (\sigma \nabla \phi) = -\nabla \cdot (\sigma \nabla E_h)$$

where  $\sigma$  is subsurface conductivity [S/m],  $\phi$  is electrical potential [V] and  $E_h$  is redox potential [V].

We hypothesize that electronic conduction does not always evolve and at times electron transfer occurs through a chain of reactions, some of which are biologically mediated. If this is the case, the rate of reactions controls the electron flux which we measure through SP. To test this hypothesis it is necessary to compare the SP signature of contaminant plumes degrading at different rates. We have chosen to do this with a numerical model.

The first portion of the model uses the Plank-Henderson equation to calculate the SP due to concentration gradients of all important ions.

$$\nabla \cdot (\sigma \nabla \phi) = -\nabla \cdot \left( F \sum_i z_i D_i \nabla c_i \right)$$

where  $F$  is Faraday's constant [A·s/mol],  $z_i$  is the valence of ion  $i$ ,  $D_i$  its diffusion coefficient [m<sup>2</sup>/s] and  $c_i$  its concentration [mol/m<sup>3</sup>].

The second portion of the model is a kinetic reaction model to calculate the concentration distribution of all important ions using initial ion distribution, ion fluxes, transport and redox reactions, similar to that of Hunter et al. (1998).

## Conclusions

The degradation of organic contaminants will only produce measurable spontaneous potential anomalies when the degradation rates are rapid. SP is therefore not generally applicable as a method for delineating organic contaminant groundwater plumes, as demonstrated by two surveys carried out in Alberta.

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