

Streaming potential and groundwater contamination

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Key Words: groundwater, streaming potential, contamination, mapping, calibration

ABSTRACT

Measurements of streaming potential can provide a means for the detection and quantification of contaminants in groundwater prior to remediation. However, laboratory determinations of specific electrolyte properties are required for an adequate analysis of the hydraulic gradient in complex situations. Data obtained for the King River in Tasmania confirm a linear relationship linking streaming potential data and hydraulic gradients. Laboratory samples at low concentration (0.001M KCl) indicate values in the range 20–80 mV/cm of water pressure, while for higher concentrations (0.01M KCl) values are less than 25 mV/cm. Similar ion concentrations are observed in the King River, consistent with field correlations indicating values for streaming potential close to 15 mV/cm. In-situ fluid samples are required for more detailed analysis of local anomalies that may be associated with variations in recharge and migration of contaminants.

INTRODUCTION

Groundwater constitutes a major national resource providing fresh water supplies in remote locations, with many communities relying completely on complex aquifer systems to satisfy part or whole of their domestic or agricultural demand. Consequently, groundwater contamination is an important problem for urban and rural development because of potential impacts on aquifer integrity, water quality, health, and protection of local ecosystems. In particular, for effective management it is essential to identify new technologies for detecting the location and extent of groundwater plumes contaminated with metals from acid mine drainage or industrial activity, or from naturally occurring mineralization.

The consequences of lowered pH in sediments include increased mobility of metal ions such as iron, arsenic, lead, cadmium, copper, and aluminium, and concentrations of these may be well above threshold levels considered safe for ecosystems (see, for example, ANZECC, 1995). Groundwater extraction may also increase intrusion into freshwater aquifers of high-salinity groundwater associated with coastal areas, or from confined aquifers commonly found in inland Australia associated with marine palaeo-sediments. This makes it necessary for thorough site evaluation to determine long-term consequences of groundwater use, contaminant mobilization in groundwater, contaminant dispersion, and remediation costs.

Several geophysical techniques (e.g., resistivity, induced polarization, frequency and time domain electromagnetics) have been developed to measure the variation of subsurface properties for mineral exploration (e.g., Telford et al., 1995). Sill (1983) discusses how these techniques may be used to determine the variation in aquifer properties (porosity, permeability) while Borner et al. (1996) have used induced polarization (IP) data to evaluate the fluid transport and storage properties in shallow environments. They determined the spectral IP response of a range of unconsolidated sediments, including sands, gravels, sandstones, and silty sands. Their data can be used to investigate the true formation factor, the cation exchange capacity, and the ratio of surface area to porosity for general aquifers.

Karlik and Ali Kaya (2001) discuss geophysical methods more specifically developed for detecting contaminated groundwater. Unfortunately, additional hydraulic models are often required to predict the associated flow rates and dispersion patterns central to risk analysis. Normally, shallow boreholes are required to provide this additional information in order to construct dynamic numerical models prior to any remediation project. Consequently, more direct methods based on observations of self-potential (SP) are attractive for predicting fluid movements. Significant SP effects (arising from the streaming potential) are commonly caused by the percolation of a fluid through porous materials such as near-surface sediments (e.g., Telford et al., 1995). However, systematic calibrations of electrolyte properties are required in each aquifer in order to predict contaminant flow rates and groundwater quality from the SP observations.

STREAMING POTENTIAL

Self-potential methods are frequently used to detect variations in the electric potential observed at the Earth's surface. Sources of self-potential fields include large-scale Earth currents due to ionospheric activity, chemical potential gradients due to redox activity, and fluid movement in porous materials. SP effects caused by fluid movements are also known as streaming potentials (derived from the zeta potential described below). Extensive reviews have been provided by Sato and Mooney (1960), Corwin and Hoover (1979), Fitterman (1979), Ishido and Mizutani (1981), and Cull (1985). More specifically, Bogoslovsky and Ogilvy (1973) investigate the role of streaming potentials in SP data, for investigations of hydraulic gradients and changes in the transport properties of aquifers.

For a two-phase assembly such as a pore water-porous matrix, the interface between the two phases usually creates a redistribution of charge in the mobile phase. In water-mineral assemblies for example, a gradational layer usually extends up to hundreds of nanometers in thickness; this division is known as the electrical double layer or Gouy-Chapman layer. The inner layer is fixed by adsorption or Coulomb forces to the grain surface, while a diffuse outer layer (while free to be transported by fluid flow in the bulk liquid) also has a higher concentration of counter ions masking the grain surface charge. The electric potential at the transition from the fixed to the diffuse layer has important consequences for electrokinetic properties, and is referred to as the zeta potential.

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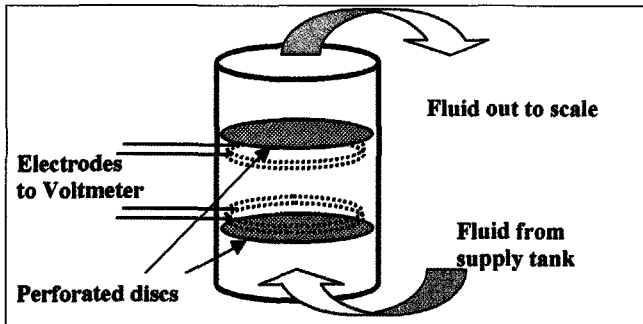


Fig. 1. Schematic of sample holder for measurements of streaming potential.

Changes to the electrical double layer, due to changes in pH and ionic concentrations, alter the charge mobility in this region, as well as the dielectric constant and dispersion (frequency dependence) of the dielectric constant. Changes to the electrical double layer also alter the zeta potential, the nominal potential at the innermost layer of the diffuse zone. In the presence of fluid movement, this layer of charge generates a potential gradient dependent on the magnitude of flow and the zeta potential. If the zeta potential remains constant, as is expected in a homogeneous aquifer, the resultant potential field (or streaming potential) is proportional to the groundwater flow. Consequently, observations of an electrokinetic effect may be used for mapping of hydraulic contours (Telford et al., 1995).

Aquifers impacted by acid rock drainage develop localized changes in hydraulic conductivity due to dissolution and precipitation of iron and copper oxy-hydroxides such as jarosite (Blowes et al., 1991). Accurate modelling of heterogeneity to predict changes to hydraulic gradients and hence movement of contaminants into uncontaminated groundwater is essential for predicting contaminant dispersion, groundwater reactions, and environmental impacts. Each of these effects can be expected to generate variations in the streaming potential observed in geophysical surveys. Consequently, SP and IP surveys are considered to show great promise in providing a mapping technique to trace the impact of surface pollutants prior to site-remediation programs.

STREAMING POTENTIAL CALIBRATION

A simple apparatus has been previously developed to investigate the nature of the observed streaming potential and the electrical characteristics of salts and metals in the groundwater flow (e.g., Ishido and Mizutani, 1981; Bogoslovsky and Ogilvy, 1972). The device designed for the current project provides a housing for granular materials, while allowing free flow of pore fluids at a range of ionic concentrations (Figure 1). This device provides for the simultaneous determination of streaming potential and zeta potential over a range of grain sizes and pore fluid chemistries, along with electrical impedance, observed using platinum electrode arrays.

Plain acid-washed quartz sand was the primary material used for the initial calibrations. This material was selected because of the relative simplicity of its surface chemistry and the availability of a consistent grade of acid-washed sand grains. Additional samples were produced from a supply of glass beads from an industrial supply of sand-blasting beads. These beads were inspected as part of an independent experiment and found to be generally regular in shape, approximately spherical, with limited fracturing.

All sample materials were subsequently acid-washed in a 10% nitric acid solution prepared from laboratory-grade nitric acid and double de-ionized water, to remove any surface contaminants and

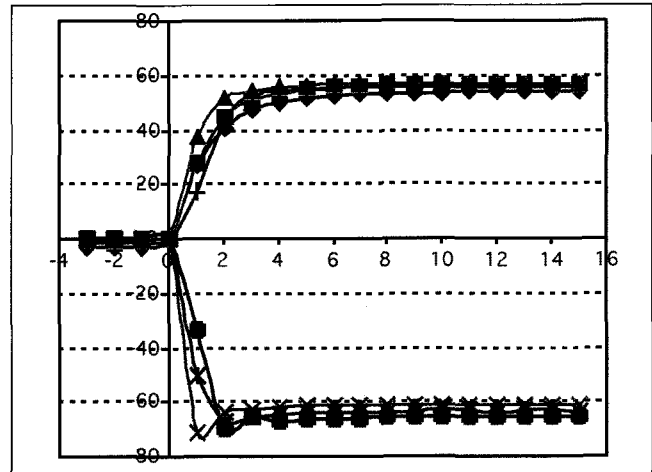


Fig. 2. Electrode potential (mV) vs. time (sec) for DDI pore fluid, pH 6, 125 Beads, (pressure drop 33 mm H₂O). Forward and reverse flow.

other soluble contaminants that may have remained. Samples were soaked overnight in the acid wash and rinsed in a double de-ionized (DDI) water bath several times. The acid wash and rinse cycle was repeated until the acid solution remained clear. Samples produced from a steel mill required additional acid-wash cycles because of the contamination of the samples with casing material. Samples were then dried at 60°C for 48 hours in a laboratory oven to remove any remaining volatile material.

The static pressure difference across the sample was determined by measurement using a steel rule to monitor the surface level of the fluid supply in the tank, the inlet and discharge elevation of the sample in the holder, and the discharge point, relative to a datum level on the table supporting the apparatus. The dynamic pressure drop across the sample was determined from the static pressure drop less the change in the elevation across the sample, effectively the height of the column in the vertical orientation. The pressure drop was assumed to be linear because of the consistent sample porosity and hydraulic conductivity. Therefore, the pressure drop between the electrodes embedded in the sample was linearly proportional to the ratio of the distance between the electrodes to the length of the sample.

Flow rate measurement was achieved by timing the mass accumulating in the receptacle on a set of electronic scales. The scales were calibrated to ± 0.0005 g with an accuracy of 0.001 g. The evaporation of fluid in the laboratory was measured as 0.3 g/minute, and was significant in low head pressure or low flow rate situations. To account for this a correction factor was included in the calculation of flow rates. Hydraulic conductivity was determined from the ratio of the flow through the sample against the pressure gradient per unit area of sample (i.e., cross-sectional area of cylinder).

The streaming potential was determined from the change in electric potential measured across the electrodes embedded in the sample when a step change in the fluid pressure gradient occurred (Figure 2). This method was arrived at after trials to determine streaming potential for a continuous flow through the sample (see also Ishido and Mizutani, 1981). After streaming potential measurements for a particular solution were completed, the electrode terminals were connected to a computer-controlled Solatron 1296 impedance analyser using fully sheathed cables in a four-electrode arrangement. This frequency analyser was used to determine the impedance of the assembly between 0.01 Hz and 1 MHz. The output of the frequency analyser provided real and imaginary components of impedance together with phase angle.

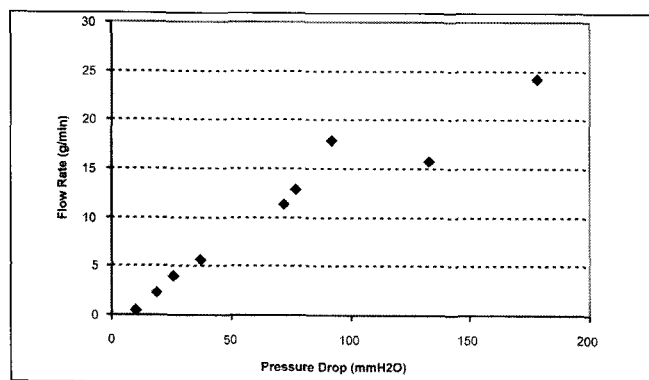


Fig. 3. Flow (g/min) vs. pressure drop (mm H₂O) through 125–250 μ m sand showing general linearity conforming to Darcy's law.

Measurements of streaming potential provide a means for the detection and quantification of flow and estimation of the hydraulic gradient. Data obtained at low concentrations (0.001M KCl) indicate values in the range 20–80 mV/cm of water pressure, while for higher concentrations (0.01M KCl) values are generally less than 25mV/cm of water pressure. These values are in general agreement with results determined from other investigations and confirm the operating principles of the experimental device. The gradient of the flow rate as a function of pressure (Figure 3) defines the hydraulic conductivity, and for the range under investigation this appears to be linear, indicating that the system follows Darcy's Law. This indicates the flow is in the laminar region over this range. While there are some minor variations in hydraulic conductivity, there is no systematic change, and the variation is likely to be due to instrument errors.

According to Darcy's Law, laminar flow through a simple porous material should have a constant hydraulic conductivity. The graph of flow rate vs. pressure drop through the material should be a straight line with a gradient proportional to the hydraulic conductivity (e.g., Figure 3). Consistent graphs of flow rate vs. pressure drop were obtained for 125–250 μ m sand samples. The values obtained show some degree of variability that is within experimental accuracy. The flow vs. pressure drop is generally linear but there is an apparent non-zero intercept. This is a measure of the effect of the end-cap and filter paper, not included in the values of the pressure drop. The accuracy of measurement of the pressure drop through the device is the main source of error for this device. Plots of flow vs. pressure drop show a range of fits to the data from very good, to moderate, with correlation coefficients (R^2) from 0.99–0.80.

Other systematic investigations indicate that the streaming potential generated during any change of the flow through the device depends on the salt concentration, the pH, the grain size, and the pressure drop at the time of change of flow. In particular, the streaming potential is dependent on solution concentration, grain size, and pH. The streaming potential for the 0.01M KCl solution decreases as the pH is decreased. A similar trend is found for the 0.001M KCl solution, and for the beads. As the electrical conductivity of the pore water increases there is also a noticeable drop in the static potential established at the grain boundary. Consequently, individual calibrations are required at each survey site to compensate for variations in electrolyte and soil properties.

FIELD SURVEYS

As an example of potential applications, we examine the environment of the King River in Tasmania. Mining operations at Mt Lyell have resulted in severe contamination of local rivers due to percolation and surface run-off from the waste products of the

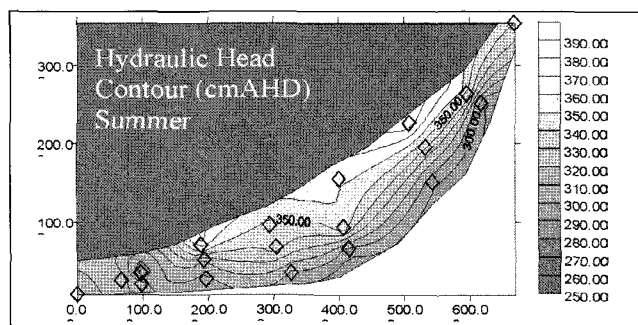


Fig. 4(a). Hydraulic contours for King River Bank.

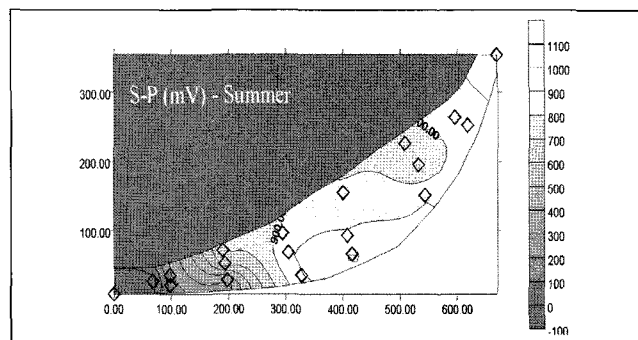


Fig. 4(b). Streaming potential equipotential contours for King River Bank.

operation. In particular, the King River has been contaminated by approximately a million tonnes of mine tailings (Koehnken, 1997; de Blas, 1992). Mine tailings at Mt Lyell are rich in copper and base metals sourced from sub-economic massive sulphide ores, spoil, and slag from the smelting operations. Subsequent leaching has contributed to the total mass loading of the adjacent river (Taylor et al., 1996; Baker and McPhail, 1998). To assist with remediation it is now essential to understand the nature of the leachate and the factors affecting mobility. Chemical and physical activity along the riverbanks is of particular concern since the riverbanks are formed from sediments including mine tailings along the King River.

The King River investigation used a total of 37 piezometers installed in a grid and nest arrangement over an area of 800 m by about 100 m long section of river bank (Baker and McPhail, 1998). Attempts to determine the groundwater flow for this investigation were limited in accuracy by the shallow nature of the aquifer, the seasonal variability of the hydraulic head, and the variability in permeability over small areas because of chemical precipitation and dissolution reactions. Approximations used by hydrogeologists to determine the groundwater flow of unconfined aquifers use the elevation of the water table as the effective head (Bear, 1972). However, this approximation is not appropriate for steep gradients near riverbanks due to the variation in hydraulic conductivity from hysteresis effects of wetting and drying cycles, saturation, and capillary pressure above the water table (Bear, 1972).

The complementary streaming-potential survey was conducted on a riverbank in the King River study area, and a typical streaming-potential contour map is compared with the piezometric surface obtained at the same time in Figure 4 (from Baker and McPhail, 1998). The contours of electrical potential are consistent with estimates of groundwater hydraulic potential (where chemical gradients were also low) and provide a means for interpolating between piezometers. However, the effects of salinity and pH on streaming-potential properties were not well understood, introducing some uncertainty in the survey.

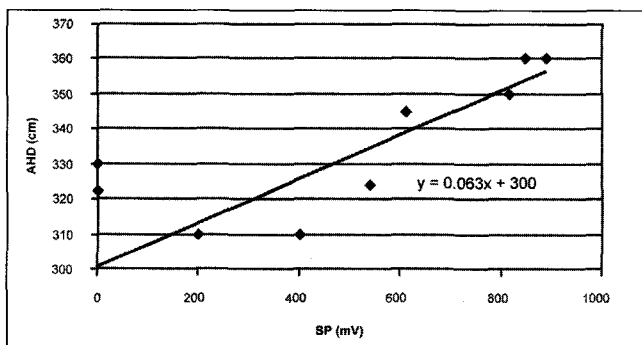


Fig. 5. Comparison of static head and streaming potential data for King River data conforming to linear relations observed with laboratory measurements, indicating values near 15 mV/cm of water pressure.

Analyses that are more detailed are now possible using the laboratory results obtained above. In particular variations in electrolyte condition and flow rates linked to ground porosity may be identified in terms of departure from the established linear relations. As an example, data from the King River are compared for a linear flow path in Figure 5. These data are essentially monotonic with a streaming potential close to 15 mV/cm of water pressure; consequently, porosities and total ion content are considered similar to the laboratory results obtained in Figure 3 (18 mV/cm of water pressure). In-situ fluid samples are required to confirm the present results, but in view of the high metal content at the King River site a comparable ion content may be expected. In view of the complex soil structure, and significant variations in recharge conditions along the river bank, new high-density SP data should provide a better indication of flow paths and contaminant anomalies than previously obtained using isolated quasi-static measurements of head level.

CONCLUSIONS

Groundwater supplies are adversely affected by discharge of contaminants from industrial sites, release of waters from landfill sites or hazardous waste facilities, and operations in mining or civil engineering projects. In particular, mining of massive sulphide deposits (and some coal reserves) may expose sulphur-rich minerals, particularly pyrite, to oxidizing environments, producing acid groundwater. In addition, there are less obvious impacts associated with earthworks (complicated by backfill removed from construction sites) and percolation of native minerals from sediments into groundwater and thereby into adjacent surface waters. Observations of streaming potential can provide an effective method for observation and mapping of these effects prior to remediation. However, an effective calibration process is required to link hydrological models with geophysical data in complex situations.

Taylor et al. (1996) have estimated mass loads on the King River from groundwater discharge of riverbanks and river delta sediments to be 10 kg of copper and 300 kg/day of sulphuric acid-equivalent, which would be a significant environmental impact in an otherwise pristine environment. However, this amounts to only 1–2% of the mass loading from the mine site itself suggesting the potential for a much greater problem. In these circumstances, estimates of groundwater flow based on piezometer data and numerical modelling are considered insufficient. More direct geophysical surveys are required to account for complex interactions along the river margins, which are subject to local transient effects in static head from variations in rainfall, flushing, and flooding.

The effects of groundwater flow, and the streaming potential developed in a range of graded sand samples and non-conductive glass beads have been investigated using a sample holder designed specifically for this project. Values were measured using a simple gravity feed from a tank containing a supply of the pore fluid to control the driving pressure. Streaming potentials measured at low concentrations (0.001M KCl) indicate values in the range 20–80 mV/cm of water pressure, while for higher concentrations (0.01M KCl) values are less than 25 mV/cm of water pressure.

The data obtained in the current study provide a sound basis for the interpretation of geophysical surveys designed for environmental audits. For example, background SP surveys have been previously conducted in Tasmania to refine groundwater flow models based on pressure gradients obtained from borehole observations (e.g., Baker and McPhail 1998). While outside the scope of the present study, new streaming potential and zeta values will allow further refinement of these models particularly in relation to local anomalies associated with the transport of heavy metals.

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