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In-Situ Measurement of Chloride Movement in Soils and Evaporative-induced changes to Soil Salinity using a new Low-cost Screen Printed Potentiometric Sensor

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INTRODUCTION

High levels of chemicals such as nitrates and chlorides have adverse impacts on water quality and the environment. Identifying the sources , transport and presence of chemical 'hot spots' in catchments is the subject of increasing research in hydrology. Conservative tracers have been widely used to provide information on chemical residence and transit times to a particular sampling point (e.g. Kirchner et al., 2010). However, to date there has been no low-cost method to continuously monitor chemical concentrations at the spatial and temporal scales required to clearly identify chemical sources and sinks in the landscape. The development and application of catchment hydrologic models to predict the impact of land use on water quality has also been hampered by the lack of high resolution spatial data (Grayson et al., 1996).

To address this problem we have developed low-cost screen printed potentiometric sensors to detect the presence of chloride ions in moist soils. In previous work (Cranny et al., 2012) we have shown that the sensors have near-Nernstian response to the concentration of chloride ions (-49.8 1.7 mV per decade) over the range 0.1 mM to 200 mM. In this report we overview the sensor design and then investigate firstly, the ability of the sensors to quantify chloride transport through a repacked soil column (45 mm diameter by 300 mm height) and secondly, their ability to detect evaporative-induced changes to the salinity of the soil solution.

SENSOR DESIGN : OVERVIEW

The sensors are manufactured by printing successive layers of functional glassy materials (Fig. 1a) fired at high temperatures (Cranny et al., 2011). A reference electrode is then used in conjunction with the chloride sensor to complete the circuit (Fig 1 b).

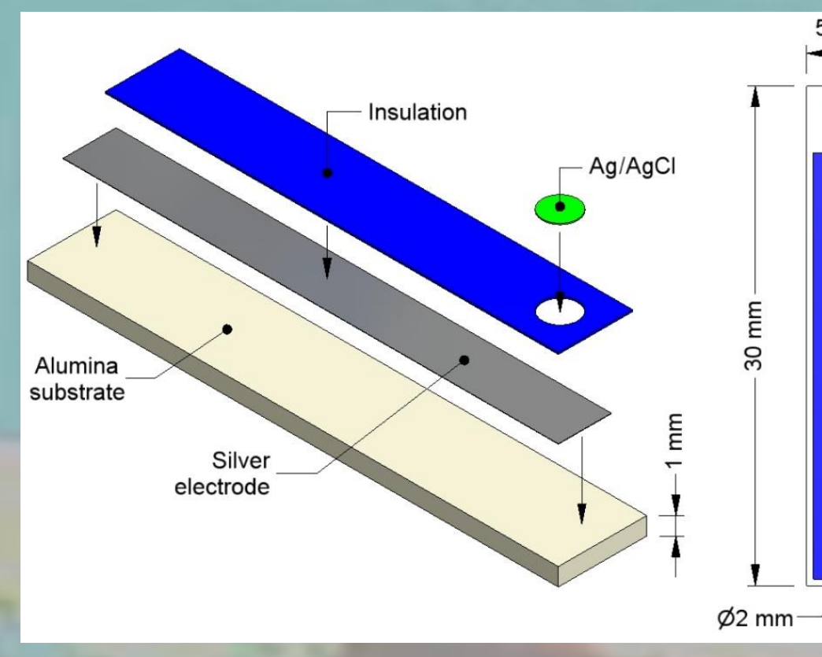
The redox reaction between silver (Ag) and its salt – silver chloride (AgCl). has a characteristic potential that is related to the activities (a) of the reactants and products, as given by the Nernst equation:

$$E = E^{0'} + \left(\frac{RT}{nF}\right)\cdot \ln\left[\frac{a_{AgCl}}{a_{Ag}\cdot a_{Cl^-}}\right]$$

Through substitution of the various physical constants at T = 25°C, conversion of activities to concentrations and by conversion of the natural logarithm term to base 10, the equation takes the form:

$$E = E^{0'} - 0.05916 \log\left|Cl^-\right|$$

Thus, the electrode potential, E, varies by approximately 59 mV per decade change in chloride ion concentration (ideal conditions).
($E^{0'}$ = the electrode formal potential and
$|Cl^-|$ = the chloride ion concentration).



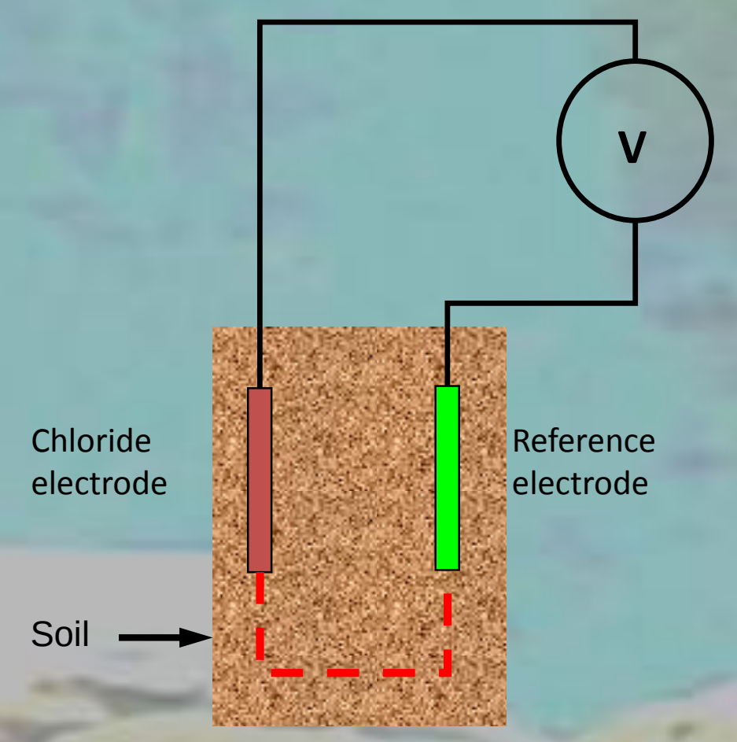


Fig. 1a. Sensor Construction. Fig. 1b. Completed Circuit.

Note that whilst it is easy to establish an electrical connection between the two electrodes (-----), an ionic connection (-----) must also be made to complete the circuit (Fig 1b).

Fig 2 shows the sensor response as a function of chloride concentration.

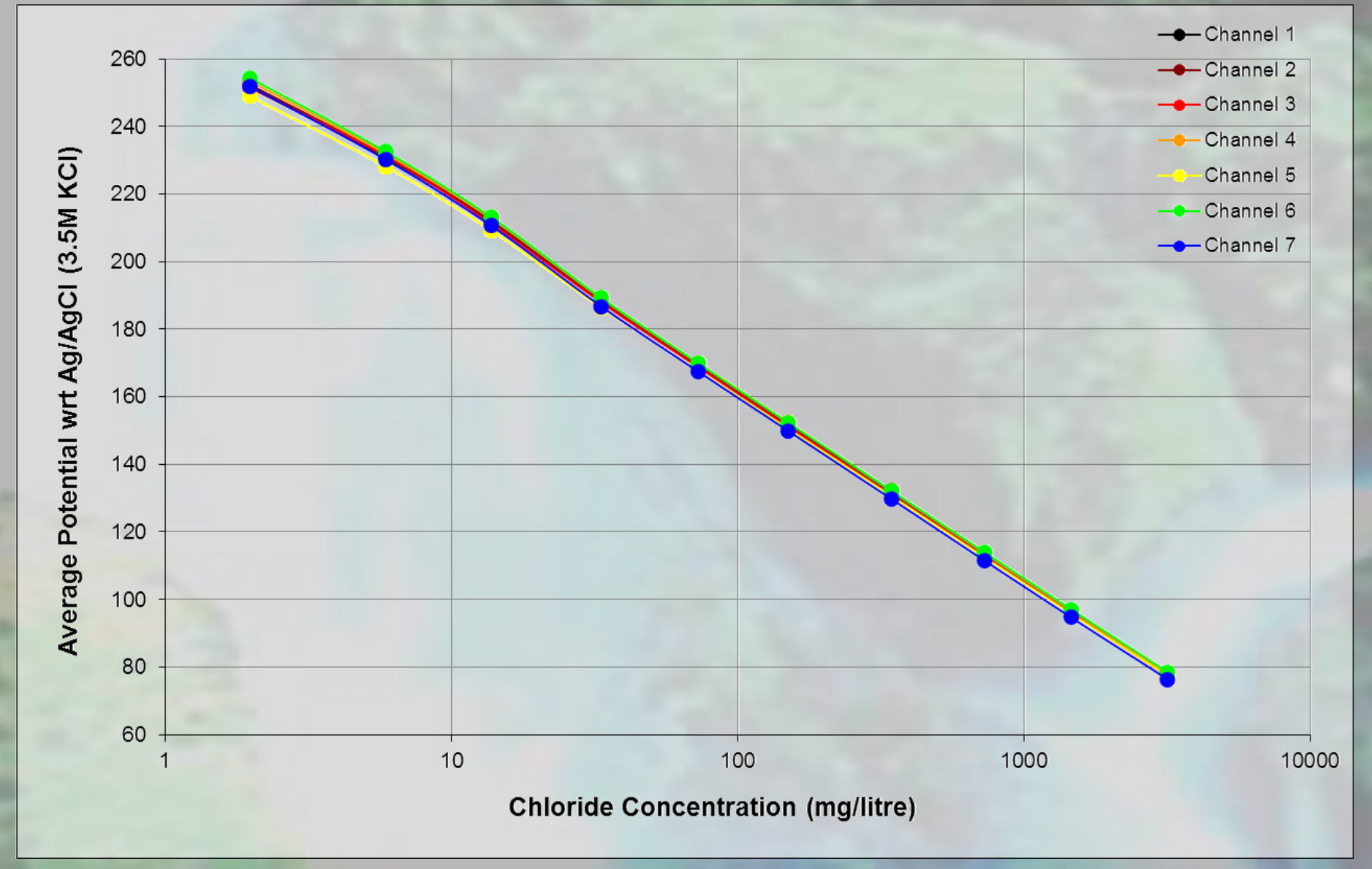
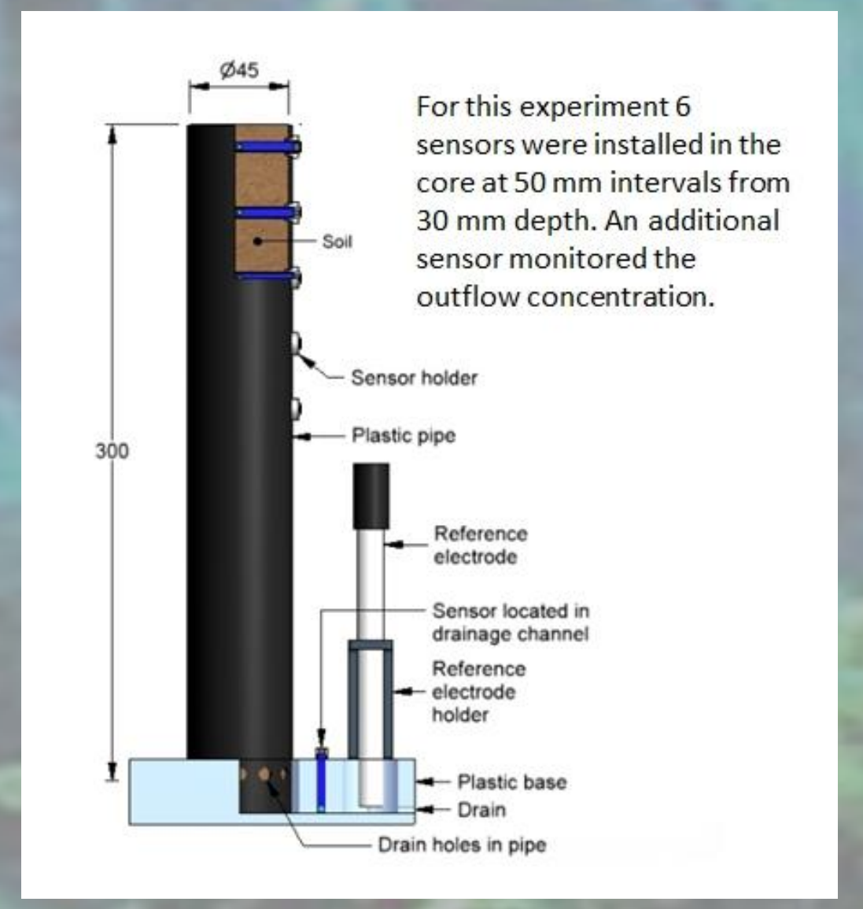


Fig 2. Sensor response as a function of Chloride concentration at 25° C. .

1) Transport of chloride through a repacked soil column under steady-state saturated flow.

The experimental setup is shown in Fig. 3. Electrode potentials were measured using a bespoke multi-channel data acquisition system based on a Libellium Waspmote wireless sensor node and a custom designed multiplexed amplifier. Data were stored on an SD memory card and also sent wirelessly using IEEE802.15.4 to a local computer for real-time monitoring through a Matlab GUI. Sensor potentials were logged at a rate of one reading per sensor every 3 seconds, with each reading being the average of 10 successive samples.

A steady-state saturated flow regime of 510 mm/h was maintained with a ponded head of 20 mm and an initial background solution of 10 mM chloride solution as NaCl. The chloride pulse was then supplied by switching to a solution of 100 mM and subsequently switching back to the background solution after 0.25 L had been supplied to the column. Results are shown in Fig.4. (a : effluent concentration fitted with CDE and b: resident concentrations vs time curves.



For this experiment 6 sensors were installed in the core at 50 mm intervals from 30 mm depth. An additional sensor monitored the outflow concentration.

Fig 3. Schematic section of soil core with sensor locations

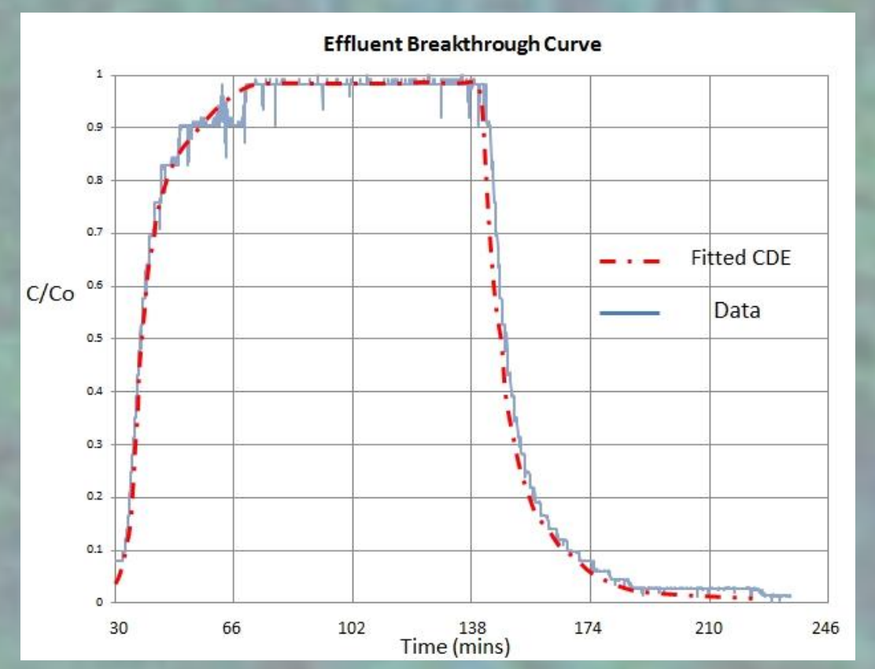


Fig 4a. Effluent BTC fitted with standard convective dispersive equation (100% mass recovery).

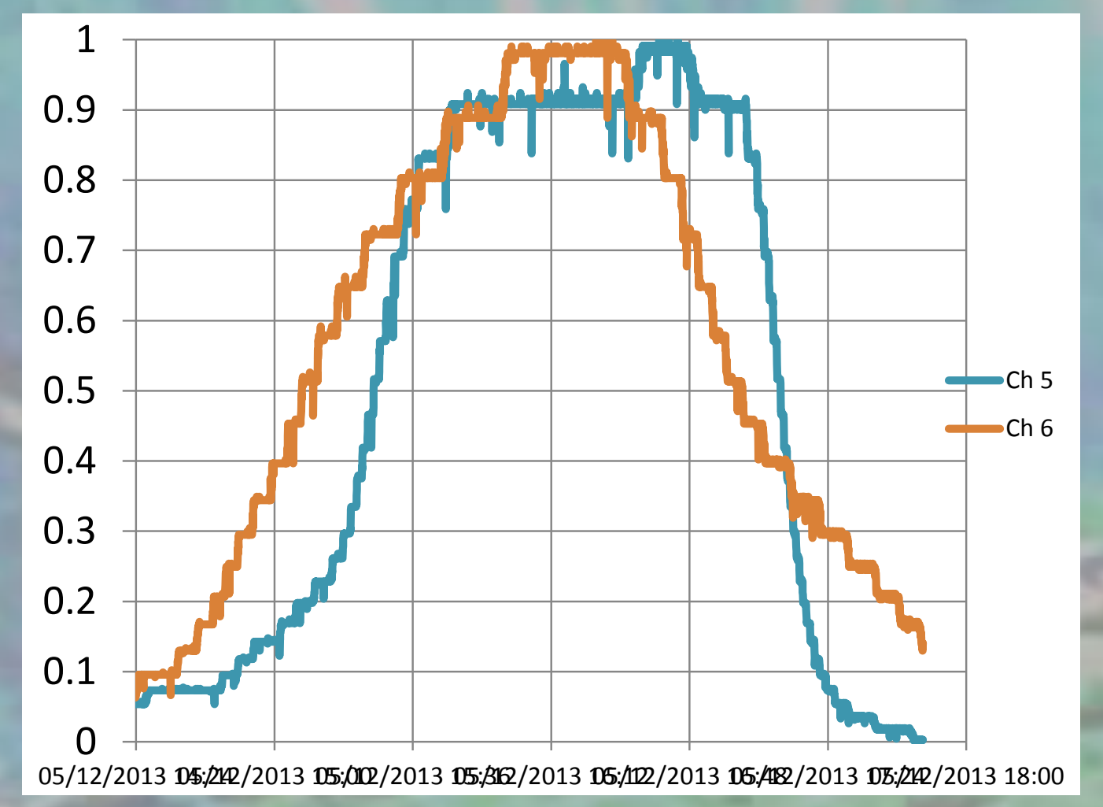


Fig 4b. Example resident concentration curves at 180 mm and 230 mm depth.

2) Evaporative-induced changes to soil salinity

This experiment was located in a glasshouse and temperature compensated. Six sensors were buried at a depth of 1 cm and a 7th was buried at a depth of 10 cm in a tub of freely-drained sand . The sand was wetted uniformly using a solution of 100 mM NaCl, and the sensor potentials were then logged for several days .

Results (Fig 5) from the final 4 days, show the shallow sensors responded in a manner consistent with the increases in the salinity of the soil solution that would have been expected as chloride moves by capillarity to the soil surface. As the soil dries; there is a daily "pulse" in chloride concentrations overlying a gradual increase in average concentrations, with the daily maxima increasing to over 750 mM chloride by the end. By contrast, potentials recorded by the 7th sensor varied little, indicating a more steady-state concentration at 10 cm depth.

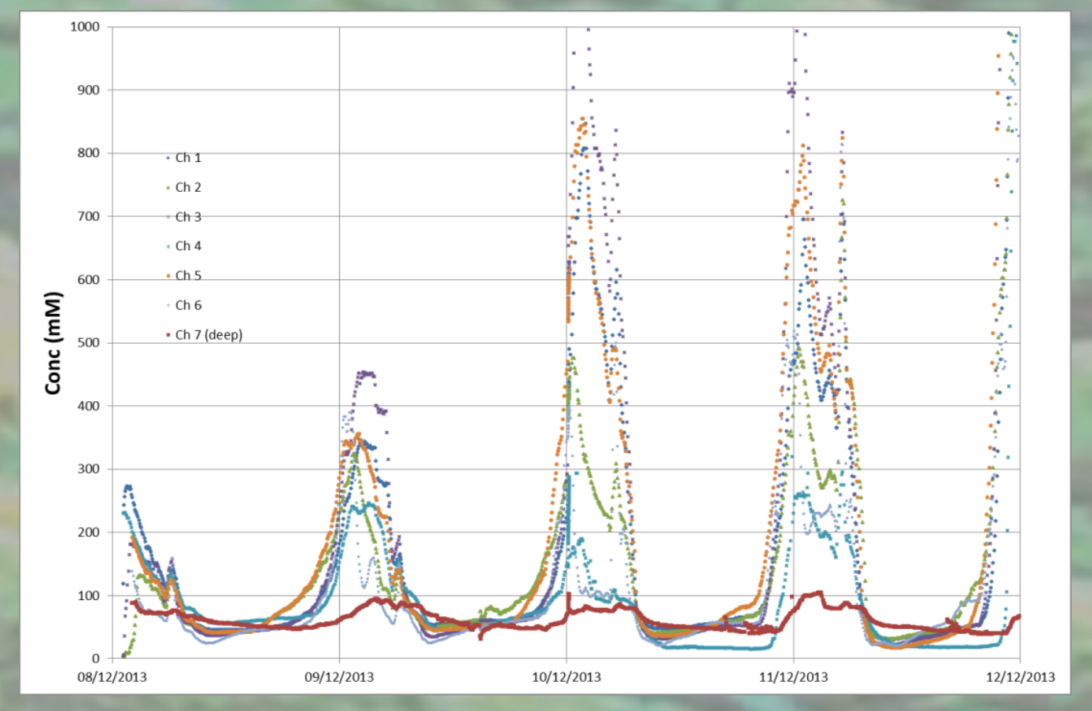


Fig 5. Last 4 days of data from evaporation experiment. Note shallow sensors indicating a diurnal increase in concentration.

CONCLUSIONS and FUTURE WORK

We conclude that the sensors provide a reliable, low cost method for use in chloride tracer studies and in directly detecting changes to the salinity of rootzone soil water.

Future work will focus on field applications coupled to wireless data transmission.

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