Applications of a Wireless Chloride Sensor in Environmental Monitoring

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Abstract—There is an established need to measure soil salinity, and wireless sensor networks offer the potential to achieve this, coupled with a suitable sensor. However, suitable sensors, up until very recently, have not been available. In this paper we report on the fabrication and calibration of a new low-cost, robust, screen-printed sensor for detecting chloride ions. We also report on two experiments using this sensor. The first is a laboratory-based experiment that shows how sensors can be used to validate modeling results by installing several sensors in a soil column and tracking the vertical migration of a chloride pulse in real time. The second is a trial of multiple sensors installed in a fluvarium (stream simulator) showing that distributed sensors are able to monitor real time changes in horizontal chloride flux in an emulated natural environment. We report on results from both surface flows as well as from sensors at a depth of a few mm in the fluvarium sediment, and differences and trends between the two are discussed. As an example of how such sensors are useful, we note that for the flow regime and sediment type tested, penetration of surface chloride into the river bed is unexpectedly slow and raises questions regarding the dynamics of pollutants in such systems. We conclude that such sensors, coupled with a distributed network, offer a new paradigm in hydrological monitoring and will enable new applications, such as irrigation using mixtures of potable and brackish water with significant cost and resource saving.

Keywords—chloride sensor, environment, hydrology, wireless sensor network

I. INTRODUCTION

Wireless Sensor Networks (WSNs) are the subject of significant research effort, and a key application area is in agricultural and environmental monitoring [1][2]. However, despite the plethora of wireless platforms [9] and protocols now available [8], one of the necessary keys to their success is being able to adequately measure the input data, and this requires suitable sensors.

Although this might seem an obvious requirement, there are other constraints necessary for a successful environmental sensor, other than just the capability of measuring the measurand. Wireless sensor networks imply many measuring points, thus cost rapidly becomes an issue, and thus sensors need to be low-cost which implies that they need to be simple. Measurands of interest in the environment generally operate over multiple scales. For example we may be interested in overall lifetimes of a decade or more, but we may also be interested in high-speed transient events within that time frame. This implies that a sensor needs a long lifetime, and in typical applications which tend to be resource constrained, this also implies the sensor needs to have low power consumption, due to power constraints, and also needs to have no maintenance requirements for the length of the deployment. Typically chemical sensor systems require frequent replenishment of consumables, or are sampling systems, which require collection of samples to be taken back to a laboratory for testing.

In this paper we will discuss a chloride sensor that is low-cost (material costs of a few 10s of Euro cents), has a long lifetime (at least a year [5], and is low-power (it is self-generating)), thus meeting all of the requirements needed for deployment in a distributed sensor network. Further we will discuss its use in a particular application, in this case salinity (defined here as an abundance of Chloride ions).

There is an established need to measure soil salinity, as this has a direct impact on the yield of crops. If salinity can be measured at a suitable temporal resolution, then irrigation applications using mixtures of brackish water and potable water become achievable [3], with a resulting saving in potable water supplies that can then be used elsewhere. An example, the irrigation system of the Harvey Irrigation Area (HIA) in Western Australia uses several reservoirs to feed the pipe network, and the water quality from each reservoir is different. Currently water rights can be traded within the HIA via an auction-based system or, more directly, between various agricultural and non-agricultural “user groups”, with one of the cost factors being the required water quality. The ability to use saline water under controlled circumstances here could both optimize water usage and lower the overall cost of water. Currently there are significant price differences for the cost of water rights depending on the source, and therefore quality, of the water by a factor of at least 500% between the lower quality water and the higher quality [4]. In order to start to make use of this, it is necessary to develop a sensor to allow
measurement of the salinity, but that is also low-cost, rugged, has low-power requirements and has a useful lifetime, as discussed above. Such a sensor, coupled with a suitable data transport and storage system, would allow near real-time monitoring and control (with suitable actuators) of irrigated land, giving significant socio-economic impact.

Currently, the usual means of making salinity measurements are by grab sampling and then analysis in a laboratory or by the use of large, expensive and isolated salinity loggers. Both of these approaches are carried out infrequently due to cost and inconvenience and only give a snapshot in time or for specific locations, potentially missing important transient or distributed events. Alternatively, conductivity can be used as a proxy for salinity, but this makes the assumption that the conductivity is only affected by changes in salinity, where in reality there are many potential interference signals (such as application of fertilizer). Thus there is a requirement for a low cost salinity sensor, which would allow interesting and high impact applications to be implemented, as in the examples above.

II. SENSOR DESCRIPTION

Recent work at Southampton has produced a prototype sensor capable of directly measuring chloride concentrations [5]. It is a potentiometric sensor, meaning it generates an electrical potential in relation to the local chloride concentration, making it inherently low power. It is manufactured by an industry-standard screen printing process which makes it low-cost, and it has a lifetime comparable with typical growing seasons.

The sensors have been reported in [5] but will be briefly described here for convenience. The sensor structure consists of a silver layer screen printed onto an alumina substrate. A patterned, insulating layer is then printed over the majority of the silver layer, which defines the active area of the electrode structure as well as leaving a short, solderable free end for electrical connection, as shown in Fig. 1. The exposed silver layer is then electrochemically chloridised, giving a silver chloride layer on top of the silver electrode. The resulting structure generates a potential that has a logarithmic response to chloride ion concentration. The response is given by the Nernst equation which predicts a sensitivity of approximately 59.2 mV per decade change in chloride concentration (pCl) at a temperature of 298 K, as given by:

$$E = E_0 - 0.0592 \log(C_{Cl^-})$$

Here E is the measured electrode potential (V), Eo is the offset potential (V) and \(C_{\text{Cl}^-}\) is the chloride ion concentration (M). Since the sensors are potentiometric, they need to be measured against a reference. Accordingly, all measurements reported here were made with respect to a commercial Ag/AgCl reference electrode (VWR GelPlas, 3.5 M KCl).

The sensors were calibrated using known concentrations of potassium chloride solution and Fig. 2 shows a typical response set for a batch of 7 sensors. It can be seen that the variability between sensors is very low, with sensitivities typically close to 55mV/pCl [5].

III. SENSOR ELECTRONICS

The logging electronics were custom built for the sensors. The system consists of an analog processing board, a digital board and a robust, water-proof housing, as shown in Fig. 3. The analog processing board allows up to 8 individual sensors to be connected and measured against a single reference. Each sensor is measured individually and sequentially through an analog multiplexer. The signal is then amplified by a gain factor which can be varied to allow for different expected dynamic ranges.

Fig. 1. Schematic showing individual layers and dimensions of sensor.

Fig. 2. Typical sensor calibration and repeatability.

Fig. 3. Schematic showing electronics architecture.
The digital board in this case is based on a Waspmote node which uses an Atmel microcontroller [6], similar to an Arduino. This platform already has interfaces for common radio systems such as 802.15.4 or GSM, and also has an SD card interface. Programming is done via a USB connection to a PC. Data is digitized from the analog board using the onboard ADC which has a 10 bit resolution. This data is then scaled, time stamped and then either assembled into a data packet for radio transmission or stored on the SD card.

For multiple data loggers operating at the same time, it is necessary to synchronize the clocks of the loggers. This is achieved by running a separate program that extracts the time from a GPS module that is temporarily installed into each logger and using this to set the real time clock. Finally the electronics are housed in a water-proof box, with the sensors grommetted through the casing. The sensors are on 1 meter cables and so the sensing points can be up to +/-1 m away from the logger. Although it is possible to construct elaborate networks with the Waspmote, for these experiments the system was either used as a simple remote logger or as a star network.

IV. EXPERIMENTS

We now report on two experiments that were carried out with the logger/sensor modules, to try and establish the usefulness and practicality of being able to measure multiple chloride points in-situ:

A) Single sensor nodes with multiple sensors distributed at different depths in a soil column.

B) Multiple sensor nodes each with multiple sensors linearly deployed in a fluvarium.

A. Single sensor nodes with multiple sensors distributed at different depths in a soil column.

This experiment is designed to show the value of making real-time measurements to validate conventional modeling predictions, which then allows other situations to be modeled with confidence. It was designed to illustrate the transport of chloride through a repacked soil column under steady state saturated flow. The experimental setup is shown in Fig. 4.

![Fig. 4. Arrangement for soil column experiment.](image)

One logger was used with six sensors placed in the soil column at 50mm vertical intervals, with the reference located in the drainage flow. In this case, data were stored on the 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 mL h\(^{-1}\) was maintained with a ponded head of 20 mm and an initial background solution of 10 mM chloride solution as NaCl. A chloride pulse was then supplied by switching to a 100 mM solution of and subsequently switching back to the 10 mM background solution after 0.25 L had been supplied to the column. As an example, Fig. 5 shows the normalized measured breakthrough curve for the top sensor, together with the theoretical curve as given by convective-dispersive modelling using an updated Excel version of the CXTFIT programme [6]. Not only is the data well matched but importantly, the mass recovery of chloride is 100% of the applied chloride.

![Effluent Breakthrough Curve](image)

Fig. 5. Measured and predicted breakthrough curve for sensor 7.

Fig. 6 shows the results from all sensors, giving absolute concentration and the progression and dispersion of the chloride pulse can be seen clearly. Some interesting observations can be made, in that there is evidence of preferential paths though the column. Some sensors do not respond in the manner that theory would anticipate, even though great care was taken in the packing of the core. For example, the trace for Channel 5 (with a rapid smooth rise and a rapid fall back to background levels) shows a profile closer to that of Channel 7 (at the top of the column) than to the adjacent channels, which show longer pulse transitions. This is probably due to preferential paths through the column. These preferential paths were verified by separate experiments using salt pulses mixed with visible dye in a transparent column, where it was seen that different paths were apparent for salt transport and that sensors only responded when the dye-laden salt reached the sensor element. This illustrates the interesting results that these new sensors can reveal in even simple experiments such as this, and also indicates that conventional point measurement data needs to be interpreted carefully.
B. Multiple sensor nodes each with multiple sensors linearly deployed in a fluvarium

A fluvarium is a form of river simulator, and in this case consists of a long channel (20 m) which had previously been filled with stream sediment. This was used as a representative stream environment. The slope of the fluvarium was adjustable, and the water flow rate could be controlled by a valved pump and measured at the outflow by the use of a flume. Fig. 7 shows a representative photo of the fluvarium along its length. The sensors can be seen inserted into the river bed at various locations. For the experiment reported here the sensors were placed at 30 cm intervals. Two sets of sensors (14 sensors) were used to give longitudinal measurements. A third set of sensors were co-located with the downstream sensors, but were located in the surface water flow rather than embedded in the bed sediment. The embedded sensors were inserted to a depth of 20 mm.

The fluvarium was allowed to soak overnight in tap water with a base concentration of 10 mM chloride. 100 ml of 100 mM chloride solution was added at the fluvarium inlet with no flow into the fluvarium and this was allowed to pool at the inlet. A sensor (sensor 2) was placed near the downstream end of this pool as a reference, and it can be seen (see Fig. 8) that the added solution was diluted by the water already in the fluvarium to give a reading of about 52 mM. The other sensors shown in Fig. 8 are those located in the river bed, moving downstream in numerical order. All of these show very low levels of chloride, except for sensor 1 which was located very near the inlet pool and this shows that there has been some diffusion of chloride though the bed, probably from previous experiments. At about 50 minutes, the gradient of the fluvarium was increased to encourage a slow drain flow away from the inlet. Periodically samples of tap water were added to the inlet pool to provide impetus. These events are listed in Table I.

V. DISCUSSION

All these events are illustrated in Fig. 8 and it can be seen that the sensor in the inlet pool responds very quickly. Sensor 1 (embedded, but nearest the inlet) also shows a small response. There is a response as the fluvarium is tilted and sensors 1 and 2 show an increase in concentration. This is due to the relatively poorly mixed inlet solution starting to move towards the outlet and move downstream. This effect is emphasised as the first volume of water is added at 107 minutes. The addition of the water pushes the higher concentration further down the fluvarium as is shown by sensor 2. Other additions are then seen to indicate a reduced concentration as the chloride slug is replaced by a more dilute solution. When the fluvarium is turned on at about 200 minutes a steady flow of water establishes itself after a few minutes and sensor 2 then shows a similar reading to the other sensors, indicating that the chloride in the inlet pool has been flushed. Sensor 1’s output continues to rise as chloride is pushed through the river bed, but starts to fall as the experiment finishes.

Fig. 9 shows the surface flow sensors located further down the fluvarium. The dotted lines show the events of Table 1. The picture is less clear here. There is evidence that sensors 1, 3 and 6 are responding similarly, showing an increase in chloride concentration with time, before tailing off. This is commensurate with the initial chloride pulse moving down through the surface flow of the fluvarium, being initially driven by the tilting and establishing a concentration gradient, as the sensors peak in inverse order of distance between 60 and 100 minutes. Later responses are driven by the water events with a time delay. The other sensors respond slowly. Visual inspection of the sensors showed that a preferred meandering flow path was being established in the fluvarium and that sensors 1, 3 and 5 were positioned in that flow. Other sensors were not in the apparent preferred flow path and so were

<table>
<thead>
<tr>
<th>Event</th>
<th>Time (mins)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>54</td>
<td>Fluvarium tilted</td>
</tr>
<tr>
<td>2</td>
<td>107</td>
<td>200 mL water added</td>
</tr>
<tr>
<td>3</td>
<td>114</td>
<td>200 mL water added</td>
</tr>
<tr>
<td>4</td>
<td>129</td>
<td>200 mL water added</td>
</tr>
<tr>
<td>5</td>
<td>139</td>
<td>400 mL water added</td>
</tr>
<tr>
<td>6</td>
<td>164</td>
<td>600 mL water added</td>
</tr>
<tr>
<td>7</td>
<td>185</td>
<td>1,000 mL water added</td>
</tr>
<tr>
<td>8</td>
<td>204</td>
<td>Flume turned on</td>
</tr>
</tbody>
</table>

Fig. 6. Calibrated data from sensors positioned in the soil pipe.
First we conclude that the sensors are useable in such environments allow some interesting observations to be noted. Extrapolating measurements from a point measurement across a wide area is established and the dangers of alternative of grab sampling. The need for distributed sensors than the expensive, time-consuming and often inaccurate to log at the same positions for longer periods of time, rather than the expensive, time-consuming and often inaccurate alternative of grab sampling. This was evident in both the slow moving soil environments. They also offer the opportunity to track short term chloride events in both flowing water, and in associated electronics offer an opportunity to measure and this result does show that in this river bed structure, diffusion of chloride from the flow to the bed was very slow, which in itself is an interesting result.

VI. CONCLUSIONS

These initial trials of chloride sensors in both these environments allow some interesting observations to be noted. First we conclude that the sensors are useable in such environments and allow accurate, real time measurements of chloride concentration in both fluid environments and also wet soil environments. Secondly, the simple experiments reported here illustrate the care needed in interpreting spot measurements in a distributed environment. Even sensors positioned a few centimetres away from a preferred flow path will give results significantly different from those in the preferred flow. This was evident in both the slow moving soil column experiment, where great efforts had been made to homogenise the soil packing, and in the more random system of the river bed. Thirdly, in the fluvarium system, although surface flows exhibited significant chloride concentrations, this is not necessarily evidenced even at low depths of 20mm in the river bed, except very near the source of chloride in this case.

Thus we conclude that these chloride sensors and associated electronics offer an opportunity to log at the same positions for longer periods of time, rather than the expensive, time-consuming and often inaccurate alternative of grab sampling. The need for distributed sensors across a wide area is established and the dangers of extrapolating measurements from a point measurement are illustrated. Thus it is concluded that these sensors, being low power and low cost, can make a significant contribution to understanding the mechanics of chloride movement though the environment and, when coupled to a distributed network, offer these results over a significant temporal and spatial scale, previously unavailable. Such richness of data can provide very useful new scientific evidence for natural system processes, but care must be taken in interpreting spot results. Future work will concentrate on adding these sensors to a wireless network infrastructure.

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REFERENCES