Assessing a Novel Method for Verifying Automated Oxidation-Reduction Potential Data Loggers: Laboratory and Field Tests

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Redox potential describes the electrical pressure of systems. In waterlogged soils, Eh is an important parameter for regulating the products of biogeochemical cycling. Until recently, Eh was measured at individual points using an electrode attached to a voltmeter. This method can overlook dynamic diel and short term fluxes in the environment. Automated data loggers enable long-term continuous monitoring of Eh in soils; however, no protocol has been developed for testing the accuracy and precision of these loggers. Automated data loggers were tested under a laboratory with known voltages to assess the ability of these units to record Eh precisely and accurately. Voltages of +450 and -450 mV were applied to four loggers with four Eh sensors five times at and voltages of +400 and -400 mV across units plus probes. The average measured voltages had an error of less than 10% and with a maximum range of ± 16 mV. The voltage averages of all units and probes were accurate within 2.5% and had a maximum range of ± 3.66 mV. Field data obtained from the automated data loggers in vegetated and non-vegetated control plots were able to record diel Eh fluxes in vegetated plots over a period of 72 hours. The loggers thus have the potential to be used to characterize in situ soil Eh conditions across larger areas and time frames than previously possible.

Introduction

Oxidation-reduction (redox) reactions are reactions involving the exchange of electrons between chemical species. Oxidation or the loss of electrons occurs simultaneously with reduction or the gain of electrons and these redox reactions comprise virtually all biological and many inorganic reactions in the soil (Bohn et al., 2001). The exchange of electrons from oxidized species to reduced ones creates an electrical potential in the soil (Mitsch and Gosselink, 2000), known as redox potential (Eh). Redox potential regulates many biogeochemical reactions in the soil (Reddy and DeLaune, 2008) and low Eh values are a distinguishing characteristic of wetland soils. When oxygen and subsequent compounds are removed from the soil, a Eh gradient is established as facultative anaerobes reduce energetically less favorable chemical species during the final stage of respiration. These gradients can be measured to better predict biogeochemical processes occurring in the soil. The standard method to record Eh of soils involves measuring the voltage difference between a Pt tipped soil electrode and a reference electrode (e.g. single-junction reference electrode - AgCl, calomel, salt bridge) inserted directly into the soil (Rabenhorst et al., 2009). The values are then read by a handheld meter and the voltages corrected to account for the specific reference electrode employed and the resulting voltages recorded as Eh. Although this method is often employed, it has several distinct limitations. Redox potential varies both temporally at scales ranging from hours to days to seasons and spatially. In measuring soil Eh, Pt tipped electrodes have been found to only characterize the conditions occurring in the 1 mm3 surrounding the tip of the probe (Fielder et al., 2007). Thus, single Eh measurements potentially overlook dynamic spatial and temporal fluxes in soil Eh. Additionally, the manual collection of data may not always be practical or possible due to site location, weather or events such as flooding. The automated nature of the new units mitigates problems associated with data collection by minimizing visits to sites and units can securely store data indefinitely if conditions do not allow for unit extraction at the specified time. Finally, since Eh is sensitive to water pressure, the mere presence of an observer near the measuring location may induce errors in the subsequent Eh measurements by increasing the pressure of water in the soil (Vorenhout et al., 2004). Although automated data loggers had been previously developed (Vorenhout et al., 2004; Rabenhorst et al., 2009; Vorenhout et al., 2011), the accuracy and precision of these units has not yet been tested. In this paper we seek to outline testing procedures for accuracy and precision, determine if the units both accurate and precise, and to field test the units to document their ability to record in situ Eh values.

Methods

In order to address these shortcomings, an automated data logger design was developed in the electrical engineering department at Mississippi State University. Data loggers were specified to support input from five temperature probes, four analog soil probes, and one reference probe and were capable of taking Eh measurements over short intervals of either one or twenty minutes. The unit was powered by three AAA batteries and recorded data on removable USB drives. After closing a circuit to measure and sending a current through the unit to take a data point, the unit would enter a "sleep mode" where the circuit would be opened, stopping current flow and data recording. This feature allowed for long-term deployment field (<10 days) by saving battery life. These units addressed the main shortcoming of standard Eh measurements by allowing Eh to be taken simultaneously at four sites in the soil column at short intervals over an extended period of time without the presence of an operator. Data could then be recovered when convenient, and, if desired, batteries replaced and the unit left to continue monitoring the site.

Standard Pt tipped soil probes were developed following the methods outlined by Wafer et al. (2004). Upon completion, the probes were connected to an Ethernet cable and temperature probe, allowing for transmission of data to the automated data logger. Single junction reference probes of either AgCl (Thermo Scientific, Waltham MA) or LD-15 construction grade reference (Castle Electronics, UK) model were also attached to Ethernet cables and a temperature probe.

In order to assess the units' accuracy and precision, four constructed units, sets of soil probes and single junction and LD-15 reference probes were tested in both laboratory and field settings. Before testing began, accepted accuracy was defined as less than 10% error from known values. Precision was determined a priori to be ± 20 mV of all other recorded points. An Ethernet test cord was attached to input channel on each unit and connected to a DC power supply (1710A 30V/1A DC Power Supply, BK Precision). Five voltages each of positive and negative 450 mV were applied to each of soil probe channel and readings were recorded. Constructed probes were then connected to the unit and five voltages each of positive and negative 400 mV were administered to each probe and results recorded. To test the ability of the continuous automated data loggers to measure voltages in an aqueous solution, two automated data loggers were set into a +225 mV ORP solution (Sensorex) as suggested by Nordstrom and Wilde (1998), with one logger using a single junction reference electrode (AgCl) and the other using a LD-15 construction grade reference electrode.

Field testing occurred in a vegetated agricultural drainage ditch located at the South Farm Aquaculture facility on the campus of Mississippi State University and in constructed mesocosms at the USDA National Sedimentation Laboratory in Oxford, Mississippi. In the agricultural drainage ditch, four test plots were set up; with above and below ground vegetation being removed in two of the four plots two weeks before testing began. Automated data logging units were deployed on November 9th, 2011 with all probes placed to a depth of 7 cm. Units were set to take measurements every 20 minutes for the 72 hour duration of the run. Mesocosms were planted with either Myriophyllum aquaticum (Vell.) Verdc. or Leersia oryzoides L. Sw. six months prior to testing and inundated one week before to probe deployment. In the mesocosms, two of the logger's four probes were placed to a depth of 5 cm and the remaining two to a depth of 10 cm in the soil. All units were set to 20 minute data recording intervals and allowed to run for 72 hours.

Results

All four units tested were found to be accurate within 10% of the accepted value and precise to within 16 mV for average measurements. Similarly, when probes were attached to the logging units, the combination of the probe and unit were accurate to 2.5% and precise (within 3.66 mV) for all probe combinations and voltage charges. In the +225 mV ORP solution, the unit equipped with the AgCl probe exceeded the accepted 10% error by up to 3 mV. In the contrast, all values recorded by the unit equipped with the LD-15 construction grade reference electrode were within ±13 mV of the expected value. Precision was within the accepted range for each unit. From these data, the continuous short interval automated data loggers were shown to be both accurate and precise under laboratory conditions.

In the agricultural drainage ditch the units took approximately 24 hours to equilibrate. In comparing the vegetated and non-vegetated plot, the vegetated plot (Figure 1) shows strong diel fluctuations in soil redox at multiple channels not present in the non-vegetated plot (Figure 2). Three of the four soil probes of the vegetated plot unit showed simultaneous increases in Eh starting between 9:00 and 11:00 AM. Interestingly, each of the three soil probes mirror the Eh changes of the others almost exactly, with only the magnitude of the change being different between the probes. In contrast, the measurements from the non-vegetated plot did not contain any pronounced diel fluxes or any trends across all soil probes.

In further testing, units deployed in the vegetated mesocosms displayed similar trends in fluctuations in soil redox were observed as the agricultural ditch's vegetated plot. Both units in the M. aquaticum (Figure 3) and L. oryzoides (Figure 4) plots showed a 24 equilibration period and strong diel fluxes. Both species showed similar fluxes in Eh, with the rise of Eh commencing at approximately 10:00 in both mesocosms. This pattern was observed occurring over two days. However, the rise in Eh was of 40 minutes longer in M. aquaticum than L. oryzoides. In both M. aquaticum and L. oryzoides mesocosms, an increase in temperature occurred nearly simultaneously with the rise in Eh. In M. aquaticum, Eh decreased as temperature decreased, while L. oryzoides had Eh increases of shorter duration and began to return to base levels before temperature began to decrease.

Discussion

Automated data loggers have been shown to be accurate, precise, and able to elucidate cycles in soils. Our observations of strong diel Eh cycles in vegetated plots may be the probes picking up the presence of oxidized rhizospheres or the leaking of oxygen from the roots (Jaynes and Carpenter, 1986; Flessa, 1994; Sorrell and Armstrong, 1994; Eriksson and Weisner, 1999; Sima et al., 2009; Pierce and Pezeshki, 2010; Dong et al., 2011). The physiological adaptation of aerenchyma of macrophytes transports oxygen from the atmosphere to soils in order to mitigate the toxic effects associated with heavily reduced soils (DeLaune and Pezeshki, 2001) creating oxic zones in anoxic environments (Nikolausz et al., 2008). In soils colonized by macrophytes, Eh cycles may be caused by daily changes in light intensity, resulting in an increase in photosynthetic activity in plants (Flessa, 1994) and the corresponding transport of oxygen to the soil by those plants thus creating oxidized rhizospheres. If standard Eh measurements were employed, this trend in Eh may not have been observed. The versatility of continuous automated data loggers allow them to be used in a wide variety of study environments, from mesocosms (Vorenhout et al., 2004; Rabenhorst et al., 2009), laboratory studies (van Bochove et al., 2002), sewage reclamation basins (Eshel and Banin, 2002) and tidal wetlands (Catallo, 1999). The use of these loggers allows for convenient collection of accurate and precise soil Eh data. These loggers can be used to describe bulk soil electrical properties in order to better characterize chemical transformations occurring in different spatial and temporal environments.

Acknowledgements

Funding for this project was gratefully provided by the Mississippi Alabama Sea Grant Consortium Award # NA10OAR4170078 and the Environmental Protection Agency – Gulf of Mexico Program Office, agreement number MX-95460110. We thank the Mississippi State Forest and Wildlife Research Center for personnel and administrative support as well as the electrical engineering students for their help in constructing the data loggers.

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Figure 1: Eh recorded by soil probes in a vegetated plot in an agricultural drainage ditch at Mississippi State University. All probes were placed to a depth of 7 cm for a period of 72 hours.

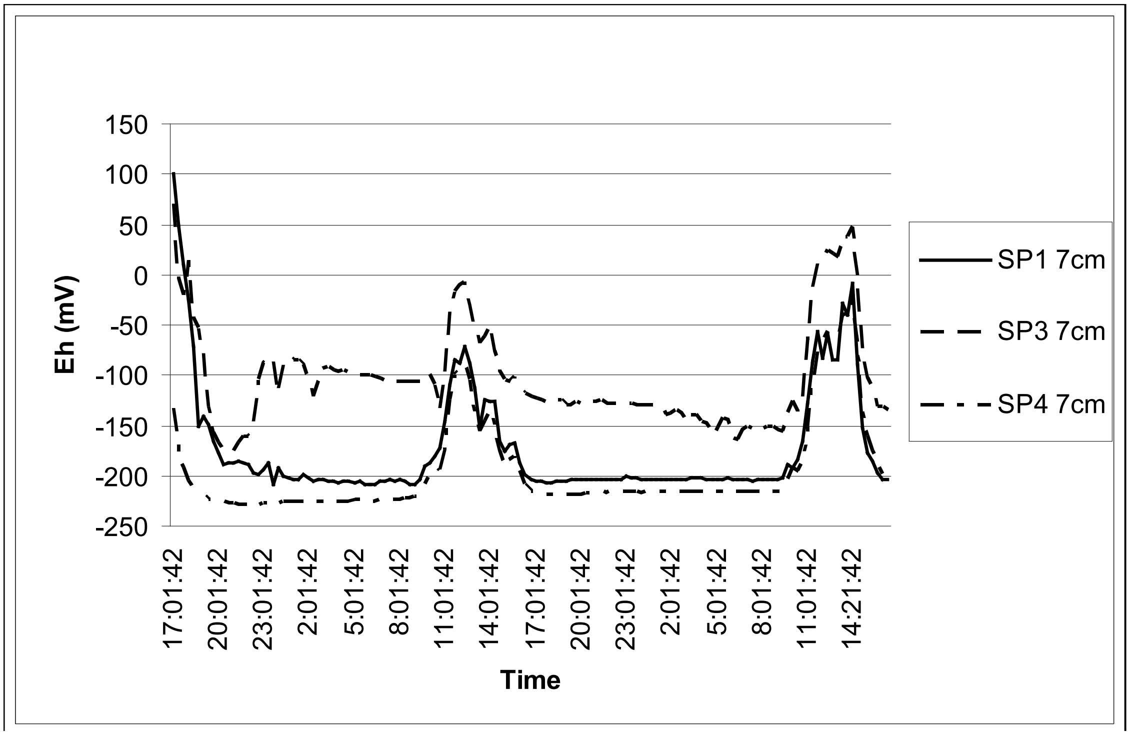

Figure 2: Eh recorded by soil probes in a non-vegetated plot in an agricultural drainage ditch at Mississippi State University. All probes were placed to a depth of 7 cm and measurements occurred over a period of approx. 72 hours.

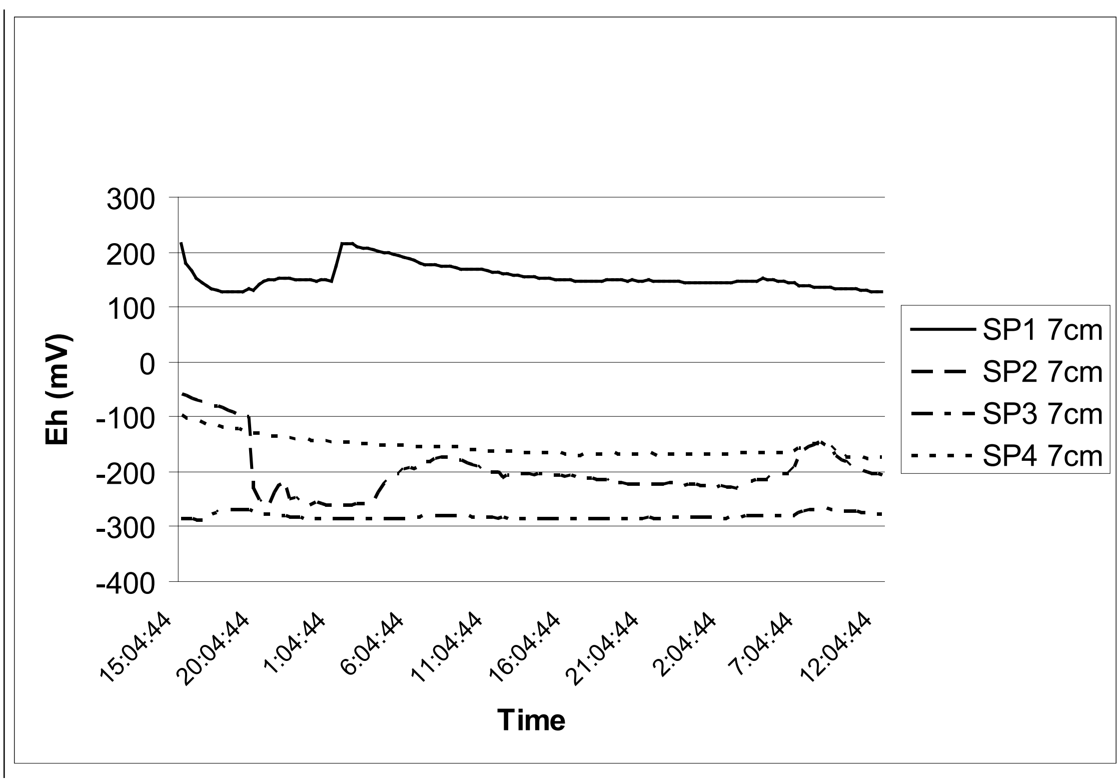

Figure 3: Eh values in M. aquaticum. mesocosms and average soil temperatures over 72 hours.

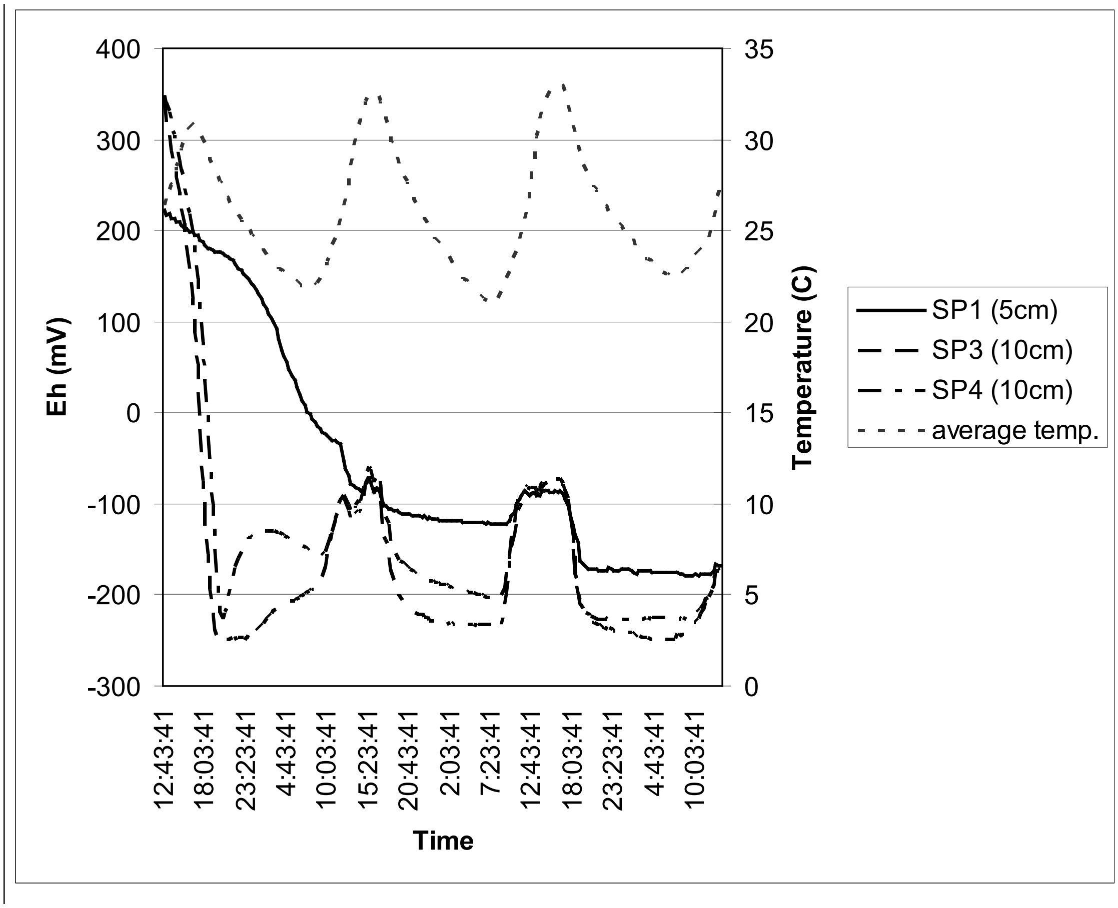

Figure 4: Eh values at 5 and 10 cm in L. oryzoides. mesocosms and average soil temperature over a 72 hour test period.