HEAVY METAL SENSING IN VEGETABLE AND SOIL SOLUTIONS USING CARBON FIBER ELECTRODE

G M Hasan Ul Banna[1], James Siegenthaler[2], Romilly Benedict[3], Wei Zhang[3], and Wen Li[1,2]*
[1]Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI, USA
[2]Fraunhofer USA Center Midwest, East Lansing, MI, USA
[3]Department of Plant, Soil and Microbial Sciences, Michigan State University, East Lansing, MI, USA

ABSTRACT
This paper reports a non-toxic, eco-friendly, and cost-effective sensing method to detect microgram per liter level of localized heavy metal ions in vegetable plant and agricultural soil solutions using glass encapsulated carbon fiber microelectrode (CFME). As a proof of principle, CFMEs were tested for sensing selected heavy metals in buffer solutions as well as plant and soil solutions using differential pulse anodic stripping voltammetry (DP-ASV). Preliminary results confirm that the CFMEs were able to measure mercury (Hg), lead (Pb), and cadmium (Cd) with a detection limit of 10 µg/L, showcasing good selectivity and sensitivity.

INTRODUCTION
Heavy metal pollution in soils is widespread in the world, resulting from both natural sources and human activities (e.g., mining and smelting, industrial emission, fossil fuel combustion, etc.). Due to their toxicity, bioaccumulation, and environmental persistence, elevated levels of heavy metals in the environment pose major threats to ecosystem health and the safety of food crops grown with contaminated soils and waters. Conventional techniques for heavy metal detection via atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS) are generally highly sensitive (with part per trillion (ppt) detection limits) and accurate [1,2,3]. However, such methods are not practical for in-situ monitoring due to their vibration sensitivity, calibration requirements, bulkiness, and costly operation. Additionally, they have high power requirements and laborious operation by specifically trained personnel.

Compared to the conventional methods, electrochemical sensors have the advantages of low cost, low power consumption, simplicity, high sensitivity, ease of operation, rapid analysis, portability and applicability for field monitoring of environmental samples. In particular, anodic stripping voltammetry (ASV) has demonstrated the capability to detect heavy metals at sub-part per billion (ppb) level, making it a promising method for field analysis. However, most commonly used electrodes, liquid Hg, are now avoided due to concerns about their toxicity, and solid electrode materials have been explored as alternatives [4]. Among different electrode materials, carbon fiber microelectrodes (CFME) are non-toxic, easy to handle, less expensive, and eco-friendly compared to typical solid metal electrodes such as Bi, Au, and Pt. However, the applications of CFMEs in environmental monitoring have been very limited. In this paper, we demonstrated, for the first time, the use of CFME to detect heavy metals in vegetable plant and soil solutions. This work will lay the foundation to develop new sensing technology for in-situ measurements of heavy metals in environments, e.g., soils, plants, and waters.

METHOD
The CFME was fabricated by inserting an unsized AS4 7.4 µm diameter (Hexcel, Stamford, CT) carbon fiber into a glass capillary. After aspiration, the capillary was pulled on a commercial puller, leaving a tapered seal around the single carbon fiber. The sensing area of the electrode was controlled by the extruded carbon fiber length and cut to ~75 µm from the edge of glass seal as shown in Fig. 1. The other side of the fiber was electrically connected using a conductive graphite adhesive to a wire for electrical connection. To characterize the device's sensing performance, the CFMEs were first tested in a 0.01 M acetate buffer (pH=5.15) solution containing 50 mM NaCl with different concentrations of heavy metals. After that, heavy metal measurements were conducted in plant and soil solutions, which were prepared by extracting fresh cut lettuce leaves and a soil with deionized (DI) water (100 grams in 1 liter each). The extracted plant and soil solutions were further diluted (1:10 vol%) with DI water, and mixed with heavy metal solutions prior to testing with CFMEs. Electrochemical measurements were performed using DP-ASV in a three-electrode mode where the CFME was used as a working electrode (WE), an Ag/AgCl as a reference electrode (RE), and a Pt wire as the counter electrode (CE). DP-ASV parameters are as follows: a plating deposition of -0.7 V for 120 s; and the voltage was ramped to 0.8 V with a frequency of 60 Hz and an amplitude of 40mV with an increment voltage of 2 mV. All the experiments were run in a custom-made Faraday cage.

RESULTS
Using a CFME, measurements were made of Cd, Pb, and Hg in the buffered solutions spiked with 100-1200 µg/L concentrations (Fig. 2). Although the Cd peak at the concentration of below 400 µg/L was not prominent, we observed prominent characteristic peaks for the other two metals, Pb and Hg, at low concentrations even at 10 µg/L range. Distinguishable peaks were observed in the DP-ASV plots obtained from the mixture solution of Cd, Pb, and Hg (Fig. 2d), demonstrating the good selectivity of the CFMEs. Fig. 3 shows DP-ASV plots for 0-1200 µg/L concentrations of Pb and Hg in the simulated plant and soil solutions, where the limit of detection (LOD) was ~400 µg/L for Hg and 200 µg/L for Pb, respectively. The electrode showed good selectivity for Cd, Pb, and Hg at the high concentration of 1200 µg/L (Fig. 4), whereas no strong signals for Cd were detected at low concentrations. The corresponding sensitivity of Cd, Pb, and Hg under different test solutions was summarized in Table 1. While preliminary, these results showed that our fabricated CFMEs are capable of detecting heavy metals in the vegetable plant and soil simulated solutions in the µg/L range. Further investigation is needed to improve the LOD and sensitivity, as well as to fully characterize the electrode's performance in plant and soil environments.

978-1-940470-04-7/HH2022/$25©2022TRF
DOI 10.31438/trf.hh2022.109

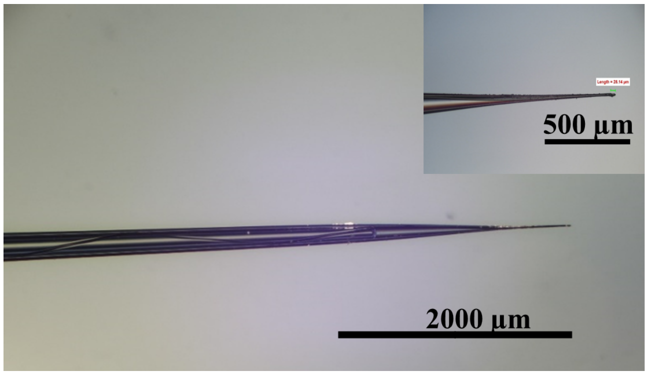

Figure 1: Microscope image of glass encapsulated carbon fiber electrode.

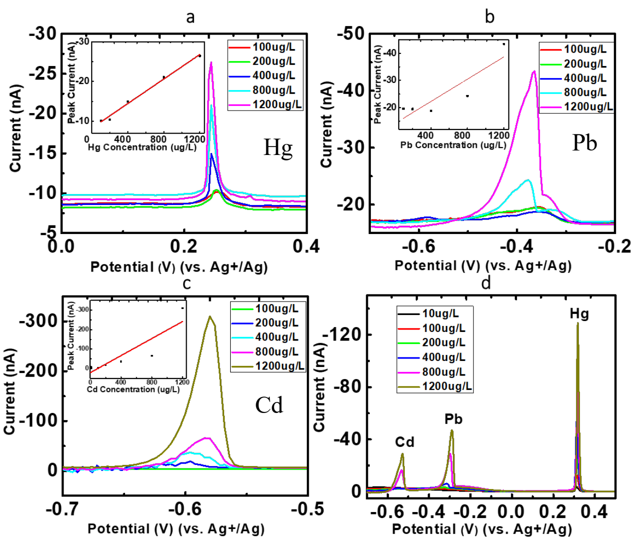

Figure 2: Detection of 100, 200, 400, 800, and 1200 µg/L concentration of (a) Hg, (b) Pb, and (c) Cd in buffer solution (pH=5.15) with CFME as WE. Insets in (a), (b), and (c) illustrate sensitivity of each heavy metal. (d) Detection in the mixture solution of Cd, Pb, Hg, each at 10, 100, 200, 400, 800 and 1200 µg/L concentration.

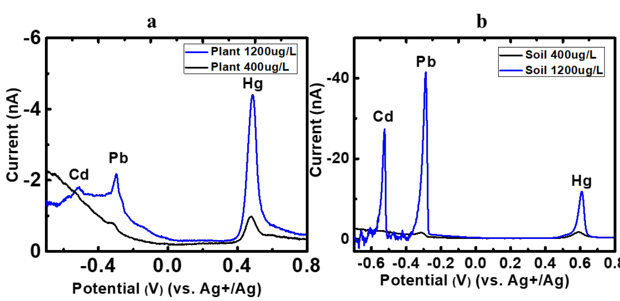

Figure 4: Detection of 400 and 1200 µg/L concentration of mixed Hg, Pd, and Cd in diluted (a) plant solution (pH=6.32) and (b) soil solution (pH=6.13) with CFME as WE.

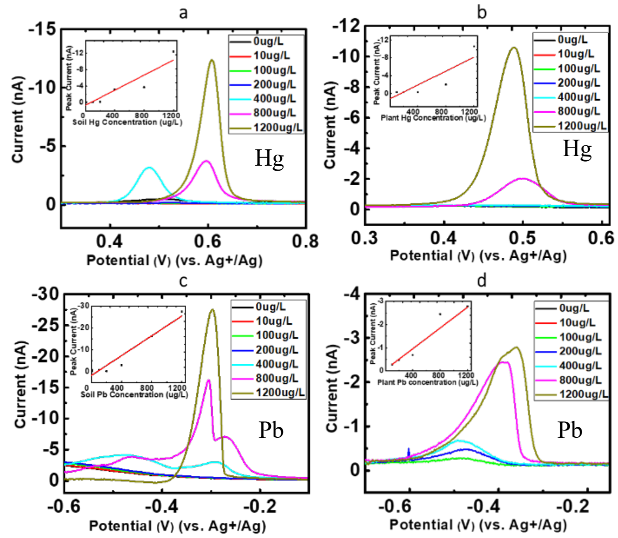

Figure 3: Detection of 0, 10, 100, 200, 400, 800, and 1200 µg/L concentration of Hg and Pb in diluted (a,c) soil solution (pH=6.13) and (b,d) plant solution (pH=6.32) with CFME as WE.

Table 1: Sensitivity of heavy metals in different solutions.

Sensitivity (nA·L/µg)	Buffer	Soil	Plant
Hg	0.01539	0.00913	0.00778
Pb	0.02059	0.02268	0.00225
Cd	0.21874	----------	----------

REFERENCES

[1] K. S. Rao, T. Balaji, T. P. Rao, Y. Babu, and G. Naidu, "Determination of iron, cobalt, nickel, manganese, zinc, copper, cadmium and lead in human hair by inductively coupled plasma-atomic emission spectrometry," Spectrochimica Acta Part B: Atomic Spectroscopy, vol. 57, pp. 1333-1338, (2002).

[2] J. Koelmel and D. Amarasiriwardena, "Imaging of metal bioaccumulation in Hay-scented fern (Dennstaedtia punctilobula) rhizomes growing on contaminated soils by laser ablation ICP-MS," Environmental pollution, vol. 168, pp. 62-70, (2012).

[3] K. Siraj and S. A. Kitte, "Analysis of copper, zinc and lead using atomic absorption spectrophotometer in ground water of Jimma town of Southwestern Ethiopia," International Journal of Chemical and Analytical Science, vol. 4, pp. 201-204, (2013).

[4] Wei Gao, Hnin Y. Y. Nyein, Ziba Shahpar, Hossain M. Fahad, Kevin Chen, Sam Emaminejad, Yuji Gao, Li-Chia Tai, Hiroki Ota, Eric Wu, James Bullock, Yuping Zeng, Der-Hsien Lien, and Ali Javey, "Wearable Microsensor Array for Multiplexed Heavy Metal Monitoring of Body Fluids" ACS Sensors 1 (7), 866-874, (2016)

CONTACT

*Hasan Banna, +1-517-619-4884; bannag@msu.edu