ANNUAL REPORT COMPREHENSIVE
RESEARCH ON RICE
March 1, 2019 – December 13, 2019

PROJECT TITLE: Determination of Arsenic Speciation in Rice and Environmental Samples

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LEVEL OF 2019 FUNDING: $19,611

OBJECTIVES AND EXPERIMENTS CONDUCTED:
California Rice Research Station, Biggs, CA

The objectives of this continuing project include: 1) to examine the binding mechanisms of As to rice roots plaques to better understand mechanisms of As bioavailability under alternate wetting and drying (AWD); 2) to characterize paddy soil samples and root plaque from previous single dry-down experiments (2017 and 2018) for their mineral composition; and 3) to explore the use of waste straw biomass, rich in silica, as a means to reduce As uptake.

To accomplish the first objective, we would analyze minerals present in iron plaque using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy by coating a the ATR crystal with these minerals and adding arsenic to elucidate the binding mechanisms. For this objective we successfully synthesize goethite and ferrihydrite (Figure 1 and 2), which are both minerals that are present in iron plaque. Figure 3 and 4 are ATR-FTIR spectra confirming the successful synthesis of these minerals.

Figure 1. Synthesis of goethite.

Figure 2. Synthesis of ferrihydrite.

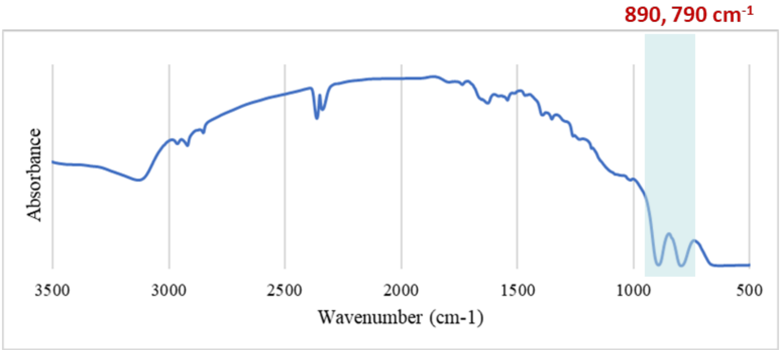

Figure 3. Goethite shows two peaks in ATR-FTIR spectra at wavenumber of about 890 and 790 cm-1.

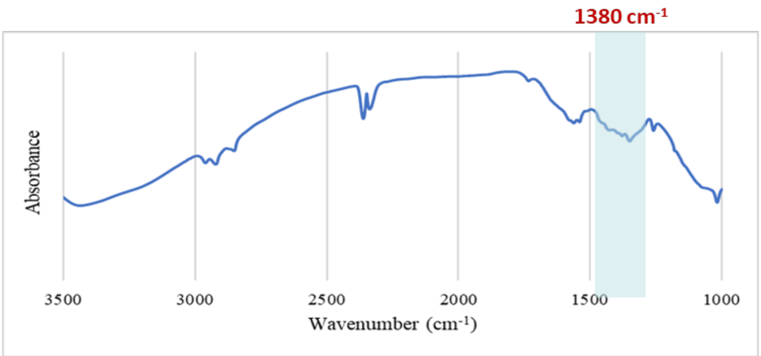

Figure 4. Ferrihydrite shows a broad peak in ATR-FTIR spectra at wavenumber of about 1380 cm-1.

For the second objective, we removed iron plaque from dry root samples by ball milling, filtering and centrifuging. Samples were then analyzed via X-ray diffraction (XRD) to determine the minerals present in iron plaque under different AWD treatments. Figures 5 and 6 reveal the differences in peaks between the Continuously Flooded (CF) treatment and the AWD treatment of highest severity (25% moisture content by volume), thus showing how AWD impacts the mineralogy of Fe-oxides in root plaque. We observe the formation of iron minerals such as goethite in both XRDs, but the AWD sample shows also other less crystalline minerals that would bind to arsenic less strongly - such as siderite, lepidocrocite and ferrihydrite. These samples are from plants at harvest of 2018 season at RES, Biggs CA; ongoing research includes analyzing the mineralogy of root plaque throughout the season.

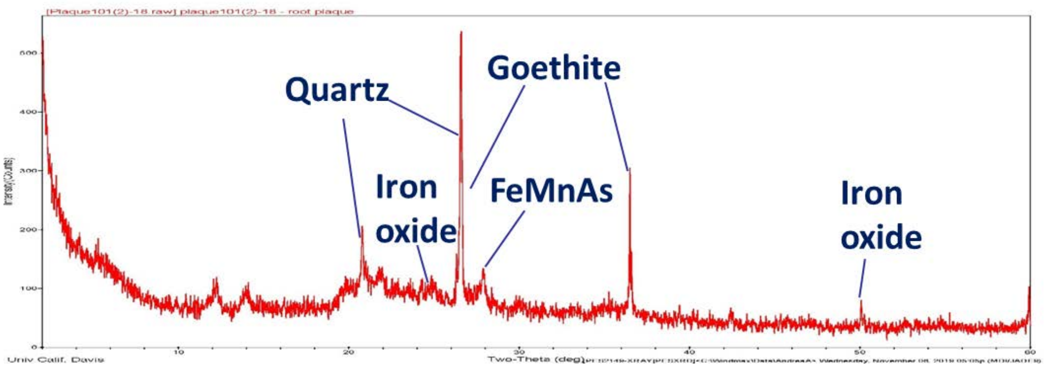

Figure 5. XRD of iron plaque in roots at continuously flooded treatment.

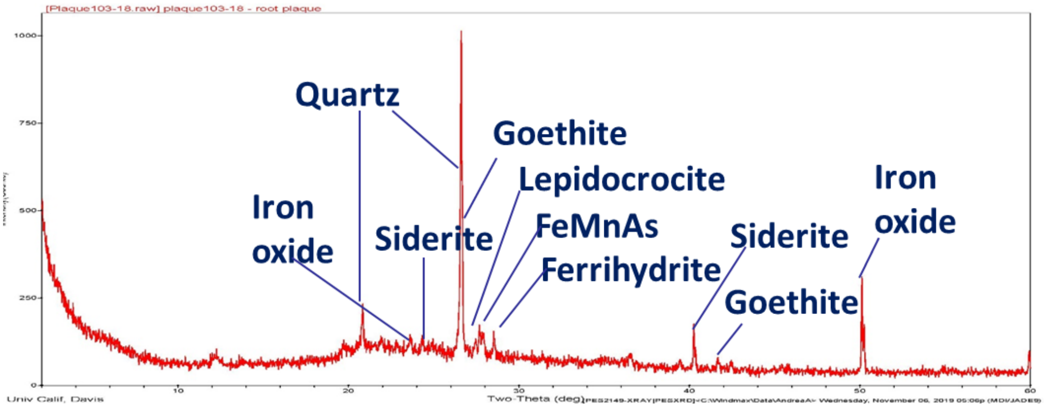

Figure 6. XRD of iron plaque in roots at high severity AWD (25% volumetric water content).

Finally, we evaluated the possibility of using magnetic biochar to remove metals and metalloids from soil, such as Cd, Pb and As. Biochar is produced through the thermal conversion of waste biomass, such as rice straw, in conditions of limited oxygen. In order to develop an economically viable option for removing metal(loids) and organic contaminants from rice paddies we examined magnetic biochar-based adsorbents with synthesized Fe_3O_4 particles embedded in a porous biochar matrix. Three production procedures were used to produce different magnetized biochar: (1) pyrolysis before magnetizing the biochar (indicated as PM treatment); (2) pyrolysis after magnetizing the biomass (indicated as MP treatment); and (3) pyrolysis conducted twice, once before magnetizing and again after magnetizing (indicated as PMP treatment). Application and separation of the adsorbent to a multi-contaminated paddy soil simultaneously removed 20 to 30% of arsenic, cadmium and lead within 24 hours (Figure 7).

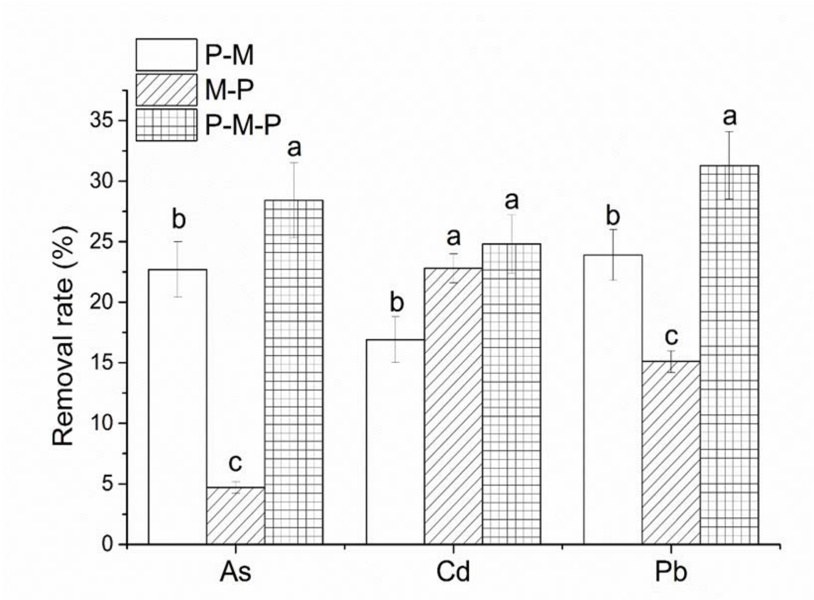

Figure 7. Removal rates of As, Cd and Pb using magnetic biochars.

SUMMARY OF 2019 RESEARCH (major accomplishments)

<u>Objective 1:</u> We synthesized iron minerals present in iron plaque and have ongoing binding experiments between these iron minerals and arsenic to better understand the interactions and uptake of arsenic in the field.

<u>Objective 2:</u> We analyzed the mineral composition of extracted iron plaque from roots of a CF and a high severity AWD treatment at harvest. Minerals that may bind easily to As were found in the AWD XRD, proving that AWD has an impact on the mineralogy of iron plaque that can affect As uptake into grain.

<u>Objective 3</u>: We mixed rice straw biochar and cedar wood chips with iron oxides to create magnetic biochar, which is a promising technology for removing contaminants from rice paddies, such as metals, metalloids and pesticides.

<u>Results from 2018 harvest</u>: AWD reduces As accumulation in shoots and grains, but can lead to increased Cd uptake. We analyzed grain samples from 2015 to 2018 and concluded that AWD does not negatively impact nutritional value for phosphorus, iron, potassium and zinc; but it slightly increased them.

PUBLICATIONS OR REPORTS:
For the current one year reporting period, the following papers were published/submitted associated with this project: 1) Wan, X., C. Li, K. Leach, S.J. Parikh. Simultaneous removal of arsenic and cadmium from soil by iron-modified magnetic biochar. Submitted - *Environmental Science and Technology.* 2) Wu. J., Z. Li, S.J. Parikh, D. Huang, X. Liu, J. Xu. Remediation of arsenic and cadmium co-contamination and its mechanism in soil by a novel calcium-based magnetic biochar. Submitted - *Journal of Hazardous Materials.* 3) Li, C. D.R. Carrijo, Y. Nakayama, B.A. Linquist, P.G. Green, and S.J. Parikh. 2019. Impact of Alternate Wetting and Drying Irrigation on Arsenic Uptake and Speciation in Flooded Rice Systems. Agric. Ecosyt. Environ. *Accepted.* 4) Carrijo, D., C. Li. S.J. Parikh. and B. Linquist. 2019. Irrigation management for arsenic mitigation in rice grain: timing and severity of a single soil drying. Sci. Total Environ. 649:300-307.

Oral reports given: 1) Aguilera et al., Agricultural and Environmental Chemistry Graduate Group annual colloquium on February 13, 2019. 2) Parikh, S.J. Evaluating biochar for agriculture and environmental applications. China Agricultural University. September 9, 2019 (*Invited*).

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:
In 2019, a number of exciting areas of research were explored to better understand how to minimize the uptake and accumulation of As in rice grains.

- We analyzed the impact of AWD on mineralogy of iron plaque in rice roots by extracting iron plaque and analyzing in X-ray diffraction, where we found that samples in CF and AWD treatments have iron minerals such as goethite, but AWD treatment forms less crystalline minerals due to the change in oxic/anoxic conditions, such as ferrihydrite. These minerals can both bind arsenic; however, the binding strength will differ, thus impacting bioavailability. We conclude that understanding the how AWD impacts Fe-oxide mineralogy in root plaques is essential for understanding how AWD impacts As uptake and accumulation in rice grains.

- We then synthesized goethite and ferrihydrite, common minerals in rice root plaques, to analyze the binding interactions between these minerals and arsenic to better understand how it is chemically interacting in the surface of rice roots. ATR-FTIR spectroscopy binding experiments are still ongoing.

- We created magnetic biochar from waste biomass (rice straw, cedar wood chips) and iron oxides to successfully bind and remove As, Cd and Pb from rice paddy soils. In our experiments, the application and separation of the adsorbent to a multi-contaminated paddy soil simultaneously removed 20 to 30% of these metal(loid)s within 24 hours. This not only is preventing As uptake into the plant during the growing season, but reducing the total amounts of As and other contaminants in the soil, which will be a benefit for subsequent years.