

MAGNETITE AND MANGANESE DIOXIDE NANOPARTICLE AMENDMENT
IMPACTS ON ARSENIC, CADMIUM, AND GREENHOUSE GAS
DYNAMICS IN PADDY SOIL

By

MARKUS W. KOENEKE

A THESIS

Presented to the Department of Earth Science
and the Graduate School of the University of Oregon
in partial fulfillment of the requirements
for the degree of
Master of Science

December 2020

THESIS APPROVAL PAGE

Student: Markus W. Koencke

Title: Magnetite and Manganese Dioxide Nanoparticle Amendment Impacts on Arsenic, Cadmium, and Greenhouse Gas Dynamics in Paddy Soil

This thesis has been accepted and approved in partial fulfillment of the requirements for the Master of Science degree in the Department of Earth Science by:

Matthew Polizzotto	Chair
Qusheng Jin	Member
Scott Bridgham	Member

and

Kate Mondloch Interim Vice Provost and Dean of the Graduate School

Original approval signatures are on file with the University of Oregon Graduate School.

Degree awarded December 2020.

© 2020 Markus W. Koeneke

THESIS ABSTRACT

Markus W. Koenke

Master of Science

Department of Earth Science

December 2020

Title: Magnetite and Manganese Dioxide Nanoparticle Amendment Impacts on Arsenic, Cadmium, and Greenhouse Gas Dynamics in Paddy Soil

Rice contamination by arsenic and cadmium is a well-documented challenge that impact billions of people globally. Our goal is to quantify the extent to which magnetite and manganese dioxide could be used as rice paddy amendments that limit As and Cd mobility and methane emissions. To do this, a suite of anaerobic and aerobic batch incubations were conducted utilizing rice-paddy soil and varying quantities and combinations of nano-magnetite and -MnO_2 . In the anaerobic incubation, As release decreased for all treatments, and Cd was not mobilized. In the aerobic incubations, all As concentrations in solutions were low and MnO_2 decreased the amount of available Cd. This research demonstrates that nanoparticle magnetite and MnO_2 can be used to reduce As and Cd mobility in flooded paddy soils, while having varying impacts on greenhouse gas emissions.

There is Supplemental Information that goes in-depth on my digestion and extraction methods, data, and other figures.

CURRICULUM VITAE

NAME OF AUTHOR: Markus W. Koeneke

GRADUATE AND UNDERGRADUATE SCHOOLS ATTENDED:

University of Oregon, Eugene, OR

North Carolina State University, Raleigh, NC

DEGREES AWARDED:

Master of Science, Earth Science, 2020, University of Oregon

Bachelor of Science, 2017, North Carolina State University

AREAS OF SPECIAL INTEREST:

Soil and Water Chemistry

PRESENTED PRESENTATIONS

1. **Koeneke, M.**, Zhang, S., Seyfferth, A., and Polizzotto, M. Iron and Manganese Amendments to Flooded Soils Decrease As Availability But Increase Cd Availability and Methane Production. Soil Science Society of America Annual Meeting, San Antonio, Texas, November, 2019. Poster presentation.

2. **Koeneke, M.**, Jones, MC., Gillispie, E., and Polizzotto, M. Elucidating the role of carbon sources on abiotic and biotic release of arsenic into Cambodian aquifers. American Geophysical Union Annual Conference, New Orleans, Louisiana, December, 2017. Poster presentation.

3. **Koeneke, M.**, Jones, MC., Gillispie, E., and Polizzotto, M. Elucidating the role of carbon sources on abiotic and biotic release of arsenic into Cambodian aquifers. Soil Science Society of America Annual Meeting, Tampa, FL, October, 2017. Poster presentation.

4. **Koeneke, M.**, Jones, MC., Gillispie, E., and Polizzotto, M. Elucidating the role of carbon sources on abiotic and biotic release of arsenic into Cambodian aquifers. North Carolina State University Spring Undergraduate Research Symposium, Raleigh, NC, August, 2017. Poster presentation.

5. **Koeneke, M.**, Jones, MC., Gillispie, E., and Polizzotto, M. Elucidating the role of carbon sources on abiotic and biotic release of arsenic into Cambodian aquifers. North Carolina State University Spring Undergraduate Research Symposium, Raleigh, NC, April, 2017. Poster presentation.

PROFESSIONAL EXPERIENCE:

Greenhouse Manager/Water Analyzer, LeapFrog Design, Current

Lab Manager, UO Soil and Water Lab, 2018

VOLUNTEER WORK

Environmental Justice Caucus Co-Chair, GTFF

Field Checker, Cascadia Wildlands

ACKNOWLEDGEMENTS

Thanks Matt Polizzotto, Qusheng Jin, and Scott Bridgham for being on my committee, assisting me on my path through this project in a countless number of ways. Special thanks to Sili Zhang, who without his help, I would have not been able to tackle a project this large. To Chelsea, Fatai, Charlotte, Jason, Katie, Rachel, Fusheng, and Gabbie, thanks for being such supportive lab mates and an overall joy to be around. I could have never done this without your support, help, love, and silliness. Thanks to Chris Russo and Jesse Muratli for all the assistance with analyzing my samples and the great conversations had on those long days. Thanks to Laura McCullough for the assistance running the GC. And lastly, thank you so much to all my friends and family who have supported and been there with me through this process. I love you all.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. METHODS	4
2.1 Sample Collection.....	4
2.2 Anaerobic Batch Reduction Incubation.....	4
2.3 Aerobic Batch Incubation.....	5
2.4 Strong Acid Digestion (EPA 3050b).....	5
2.5 Sequential Extraction.....	6
III. RESULTS	8
3.1 Characterization of Soils.....	8
3.2 Experiment 1: Anaerobic Incubation.....	8
3.2.1 Arsenic Dynamics in Soil.....	8
3.2.2 Cadmium Dynamics in Soil.....	9
3.2.3 Soil Carbon Emissions.....	10
3.2.4 Comparing Treatments	12
3.3 Experiment 2: Aerobic Study	13
IV. DISCUSSION.....	15
4.1 Anaerobic Study	15
4.2 Oxidic Study	16
4.3 Future Challenges	16
V. CONCLUSION.....	18
REFERENCES CITED	19
Supplemental Information	

LIST OF FIGURES

Figure	Page
Figure 1 – Anaerobic experiment arsenic release	9
Figure 2 – Anaerobic experiment cadmium release	10
Figure 3 – Anaerobic experiment methane emissions	11
Figure 4 – Anaerobic experiment carbon dioxide emissions	11
Figure 5 – Week 8 anaerobic experiment data compared.....	12
Figure 6 – Aerobic experiment As and Cd released	14

I. INTRODUCTION

Rice is the most important food in the world for human consumption, with approximately 4 billion people relying on it as a staple food (1). Several challenges currently jeopardize global rice production, one being the accumulation of arsenic (As) in rice grain, which poses threats to human health (2). This challenge has been exacerbated by farmers using As-contaminated groundwater for irrigation, causing an increase in As concentrations in rice paddy soils and rice (3). Many solutions have been proposed to address this challenge, but there are other environmental quality and human health issues that can arise or be intensified. Some of these issues are increasing methane (CH₄) emissions (4), cadmium (Cd) accumulation in rice grain (5), or a decrease in iron (Fe) and manganese (Mn) micronutrients in rice. Therefore, solutions are critically needed that comprehensively address all of these problems.

Varying solutions have been proposed to address these challenges, however each solution comes with complicating factors that can decrease the overall utility of that solution. Alternate wet-dry irrigation (AWD), where rice fields are drained to oxygenate the system, decreases As and Fe uptake, yield, water use, and CH₄ emissions, but increases Cd uptake and N₂O emissions (6-9). Silicon amendments, typically in the form of rice straw, rice husk, rice straw ash, and rice husk ash, have shown very promising results in decreasing As uptake by rice. This is due to many species of As and Si sharing a pathway for uptake into rice, which Si is prioritized for (10), with the exception of dimethylarsenic acid, which increases in grain concentration with this amendment. In flooded paddy soils, rice with husk amendments took up 45% less As and reduced CH₄ emissions, and in non-flooded paddy soils, rice took up 40-50% less Cd attributed to increasing pH and biomass content (11, 12). Biochar formed from the rice husk is another possible solution to this challenge that is promising. Studies have shown increases and decreases in both As, Cd and CH₄ depending on how the biochar is made and manipulated (13)(14). Biochar can also decrease zinc, a micronutrient, uptake by rice and stimulate direct interspecies electron transfer, which can increase methane emissions, though it is poorly

studied. (14)(15). The strategies stated above are useful for achieving certain objectives with growing rice, however they can also threaten rice or environmental quality.

Iron and manganese oxides are two oxide minerals that impact redox chemistry and contaminant sorption, which suggest they can be used to solve As and Cd issues (16). Iron- and Mn-oxide amendments have been used to varying success on limiting As and Cd uptake by rice. Both Fe- and Mn- oxides have the ability to scavenge contaminants like As and Cd in soil and can keep them bound in the soil (17). Iron-oxides readily sorbs As, but, it can be reduced in a flooded system, which mobilizes the sorbed As (17). Manganese-oxide is a powerful oxidant, that can oxidize As(III) to As(V), Fe(II) to Fe(III) and sorb cations (18). Cadmium plant uptake occurs through the Fe(II) and Mn(II) transporters, so amendments could prevent mobilized Cd from being taken up by rice. Their reactivities and ability to sequester contaminants vary according to the specific oxide mineralogy, surface chemistry, and surface area.

In the present study, we utilize nanoparticle Fe- and Mn-oxides to examine their utilities as soil amendments. Nano Fe- and Mn-oxides size can be orders of magnitude smaller than their bulk counterparts, resulting in reactivities, structures, and mobility in soils exceeding those of their bulk counterparts (19). Their small size results in very high surface areas and unique surface structures that can make them more reactive or act differently in the environment to the bulk-oxides. They have the ability to get into pore water and have a higher impact on contaminant sorption and reduction potential (19). In particular, nano-magnetite is an Fe-oxide that is very effective at sequestering As, and in reduced environments, when most Fe-oxides would undergo reduction and release the As back into solution, magnetite does not (20). Nano-MnO₂ is a mineral that has been successfully shown to mitigate As accumulation in rice from a contaminated field through sorption and oxidation of Fe(II) to form Fe(III) oxides (21). No studies have looked into the impacts that both nano-magnetite and nano-MnO₂ have on arsenic, cadmium, and greenhouse gas emissions (GHG).

The overall goal of this work is to utilize magnetite and manganese dioxide as soil amendments to limit As and Cd mobility and monitor methane and CO₂ emissions. To accomplish this goal, we examined the impacts of magnetite and MnO₂ nanoparticle amendments on As and Cd mobility and availability and GHG emissions in oxic and anaerobic rice paddy soil incubations. Overall, we found that magnetite and MnO₂ can be effective at limiting As and Cd mobilization and greenhouse gas emissions in oxic and anaerobic environments, although specific results are dependent on amendment concentrations.

II. METHODS

2.1 Sample Collection

Bulk soil samples were collected from the University of Delaware RICE farm in Newark, DE, USA and shipped to Eugene, Oregon aerobically. The farm was naturally a grassland and the soil is an Udisol/Acrisol.

2.2 Anaerobic Batch Reduction Incubation

A 2-month batch incubation experiment was conducted to assess how Fe and Mn nanoparticle treatments impact reduction potential and As and Cd dynamics in farm soils. The method was adopted from Gillispie et al. 2016 (22), and modified for this experiment. Two and a half grams of soil were added to 30 mL serum vials for 3 different treatments. The three treatments were a 50 nm manganese dioxide nanoparticle (US Research Nanomaterials Inc.), a 15-20 nm magnetite nanoparticle (US Research Nanomaterials Inc.), and a combination of the MnO₂ (Mn) and magnetite (Fe) nanoparticles. Each treatment had 3 different concentrations, 0.025 g, 0.075 g, and 0.125 g, for 5 sample dates where each date has a specific sample for it, in triplicate. Each sample was destructively sampled, so every vial was unique for each sample date, treatment, and replica. The solution was purged of oxygen by boiling 18 mΩ water and bubbling N₂ through it, and contained HEPES buffer, a minimally reactive buffer to a pH around 6, and 10 mM potassium chloride (KCl) as an electrolyte. Samples and solutions were brought into an anaerobic chamber, purged with nitrogen (92%) and hydrogen gas (8%) to remove oxygen, and 25 mL solution was added to each sample. Soil-free controls and blanks were included in duplicate, where treatment in the soil free controls was 0.075 g for Fe and Mn. Vials were crimp sealed in the anaerobic chamber, taken out of the chamber, and set up on shakers covered in tinfoil until sample day.

On sample day vials were taken off the shaker and headspace concentrations of CO₂ and CH₄ were analyzed by gas chromatography (GC) using a flame ionization detector

equipped with a methanizer (SRI Instruments, Torrance, CA, USA). For GC analysis, the instrument was calibrated using a mixed CO₂ and CH₄ gas with a calibration range of 1,010-10,100 ppm CO₂ and 99.9-999 ppm CH₄. After samples were analyzed for gas they were brought back into the anaerobic chamber. In the anaerobic chamber samples were measured for Eh and pH, decanted into 50 mL centrifuge tube, centrifuged at 4,000 rpm for 10 minutes, decanted into a 50 mL syringe, pushed through a Thermo Scientific PTFE 0.2 um filter, and then acidified with 5 drops of 12M HCl. Sample vials with the soil inside were left in glovebox to air-dry in an anaerobic environment. Solutions were taken out of the glovebox and refrigerated at 4°C. For Fe, Mn, As, and Cd solution analysis, samples were diluted at a 2:5 ratio in 2% HNO₃, then taken to Oregon State University's W.M. Keck Lab. Iron and Mn were analyzed via ICP-OES (Spectros Arcos II), and As and Cd solutions analyzed on an ICP-MS (Thermoscientific iCAP-RQ).

Water content of the soil was calculated by weighing out 2.5 grams of soil, done with 6 replicates, putting them in an oven at 105°F for 24 hours, taking them out and reweighing the dry soil.

2.3 Aerobic Batch Incubation

A follow up 2-month batch incubation experiment was conducted to assess how Fe and Mn nanoparticle treatments impact As and Cd dynamics in an aerobic farm soil. The same method for the anaerobic study was used for this one with a few changes. Only one amount, 0.025 g, of amendment was used, the water for the solution was not purged with nitrogen, samples were set up outside of glovebox, and covered in parafilm with slits for oxygen exchange. Because of this there was no gas analyses done at the end of the study. Samples were processed, stored, and analyzed the same way as the aerobic study.

2.4 Strong Acid Digestion (EPA 3050b)

The soil used for the experiment, and soils from week 8 samples, were analyzed for Fe, Mn, As, and Cd after they were acid digested following the EPA 3050b protocol. This

shows the “environmentally available” but does not dissolve silicate structures. For the digestion, 0.5 g of wet soil was weighed and put in a 50 mL digestion tube. Two and a half milliliters of 18.2 MΩ water and 2.5 mL of 15.8 M Nitric Acid (HNO₃) were added to tubes and the samples were vortexed. The samples sat over night for 16 hours in the acid covered with a watch glass. After the 16 hours, the samples were heated to 95°C in a DigiPrep Digestion Block for 15 minutes then removed from heat to cool for 10 minutes. After cooling, 2.5 mL of 15.8 M HNO₃ was added to samples, then they were vortexed, and tubes heated to 95°C for 30 minutes. This step was repeated once. After the repetition, watch glasses were removed and tubes were heated to 95°C for 2 hours. Following the 2 hours the samples are removed from the heat to cool. Once cooled, 1.5 mL of 18.2 MΩ water and 1 mL of 30% hydrogen peroxide were added to samples. Samples were then put back in the digestion block with watch glasses on and heated to 95°C, adding 1 mL of 30% hydrogen peroxide when the effervescence stopped from the previous addition. This was done until 5 mL total of 30% hydrogen peroxide had been added to the samples. Once the effervescence of the 5th mL of 30% hydrogen peroxide stopped, samples were vortexed and heated uncovered to 95°C for 2 hours. After the 2 hours, samples were taken off the digestion block and left to cool. Once cool, 2.5 mL of 12 M hydrochloric acid (HCl) was added to samples, then samples put back on digestion block and heated to 95°C for 45 minutes. Samples were taken off of the digestion block, cooled, filtered with Whatman paper #41 into 50 mL centrifuge tubes and stored in the fridge. Samples were analyzed for As, Cd, Fe, and Mn via ICP-MS and ICP-OES, as described above.

2.5 Sequential Extraction

The chemical fractionation of solid-phase Fe, Mn, As, and Cd was achieved via sequential extraction adopted by Keon et al at 2001, modified with the addition of a step for chemical fractions associated with crystalline Fe oxides (Mehra and Jackson, 1960) and without the monosodium phosphate step (Detailed in Supplemental Information). The extractants and steps detailed below target Fe, Mn, As, and Cd from (1) ionically bound,

(2) Mn-Oxides (3) amorphous iron oxide, and (4) crystalline iron oxide.

1. 1 M MgCl_2 , pH 8, 2 h, 25 °C two repetitions + one water wash

2. 1 N HCl, 1 h, 25 °C one repetition + one water wash

3. 0.2 M ammonium oxalate/oxalic acid, pH 3, 2 h, 25 °C in dark
one repetition + one water wash

4. Citrate-bicarbonate-dithionite (from Mehra and Jackson, 1960)

III. RESULTS

3.1 Characterization of Soils

Data in Table S1, obtained through digestions and extractions, show associations between elements in the soil. These strong acid digestion data show the original soil had 881 mg/g Fe, 13.1 mg g⁻¹ Mn, 227 ng g⁻¹ As, and 3440 ng g⁻¹ Cd. The soil has a pH of 6.67 and a wet-dry-ratio of 1.34 g : 1 g.

3.2 Experiment 1: Anaerobic Incubation

3.2.1 Arsenic Dynamics in Soil

Across all incubations, As release from soil to solution was greatest for samples not treated with Fe or Mn nanoparticles (Figure 1), with nearly 500 ng As released per g soil, or roughly 9% of the total As in the soil (6 ug g⁻¹, Table S1). In contrast, only 165 ng As per g soil was released in incubations with added nanoparticles, excepting the 1% and 3% MnO₂ amendments, where 400 ng g⁻¹ and 300 ng g⁻¹ As released, respectively, by day 28. For all treatments, As release primarily occurred in the first 28 days, after which dissolved As concentrations stabilized or slightly decreased. Magnetite amendments appeared to have the greatest inhibition of As release, as shown in Figures 1a and 1c, whereas MnO₂-only treatments resulted in As release that approached levels observed without nanoparticle addition through 28 days (Figure 1b). However, by 8 weeks of incubation, As release was below 165 ng g⁻¹ in all treatments (Figure 5c). Finally, As release generally was lessened with increasing nanoparticle concentration for all treatments.

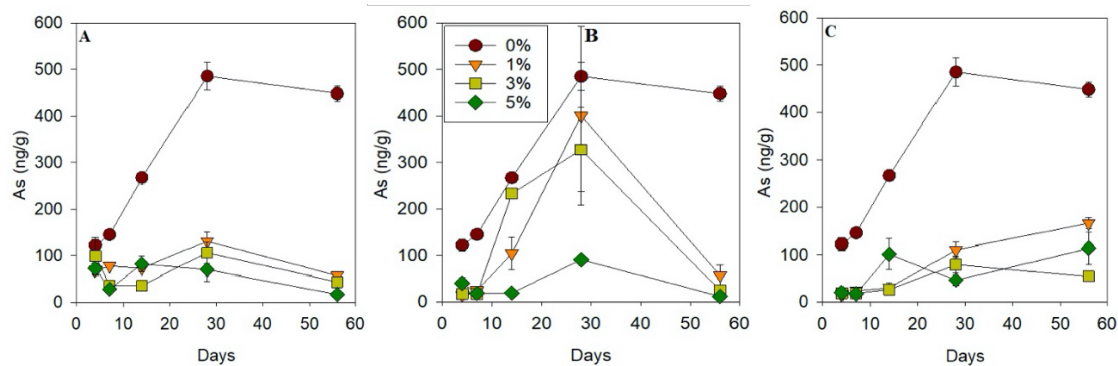


Figure 1: Anaerobic experiment arsenic release per gram of dry soil from magnetite treatment (A), from MnO₂ (B), and from a combination of both magnetite and MnO₂ (C). Error bars represent standard error of experimental triplicates.

The digestion and extraction data of the post-experiment week 8 anaerobic incubation soils are shown in Table S2. The strong acid digestion released 6.47-7.51 ug g⁻¹ As from the soils. The ammonium oxalate/oxalic acid (AMO), hydrochloric acid (HCl), and citrate-bicarbonate-dithionite (CBD) extractions released between 0.6-3.7 ug g⁻¹ As. All magnesium chloride (MC) extractions released a maximum of 0.23 ng g⁻¹ As.

3.2.2 Cadmium Dynamics in Soil

Across all incubations Cd release from soil to solution was low, with highest values in samples treated with Fe or Mn nanoparticles (Figure 2). The range of Cd released over 8 weeks was 2-6 ng Cd released per g soil, or roughly 0.05-0.15% of the total Cd in the soil (4260 ng g⁻¹, Table S1). In contrast, samples that did not receive a treatment released less than 1.6 ng of Cd per gram of dry soil across the entire experiment. The highest concentrations of Cd released occurred at 56 days for the 5% magnetite amendment, 14 days for the 5% MnO₂ amendment, and 56 days for the 5% magnetite/MnO₂ treatment. These were the only samples that released over 3.15 ng of Cd across the incubation. For the magnetite amendment, the majority of the Cd was released after 14 days, with the exception of the 5% amendment, which released 1.63 ng Cd per g soil over 14 days. For the MnO₂ amendment, there is a spike in cadmium that occurred between 7 and 14 days, with Cd release being 2.33- 5.65 ng per gram of dry soil, and increasing with amendment concentration. However, by 28 days, Cd levels lowered to 1.4-2.6 ng Cd per g soil, and

those levels plateaued through 56 days. For samples treated with magnetite/MnO₂, Cd release primarily happened between 7 and 14 days to 1.3-2.6 ng per g soil, which plateaued through 28 days, and slightly increased through 56 days to 2.2-3.6 ng per g soil.

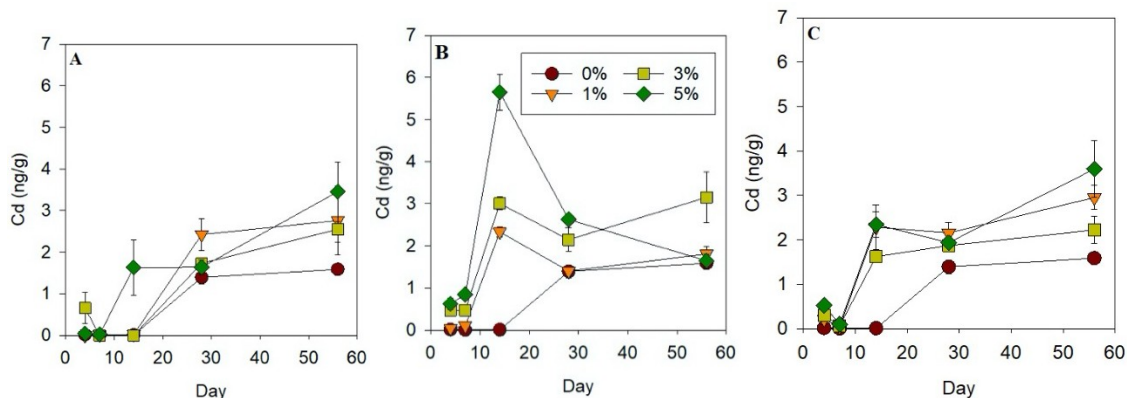


Figure 2: Anaerobic experiment cadmium release per gram of dry soil from magnetite treatment (A), MnO₂ treatment (B), and Fe/Mn treatment (C). Error bars represent standard error of experimental triplicates.

The digestion and extraction data of the post-experiment week 8 anaerobic incubation soils are shown in Table S2. The strong acid digestion data of released Cd ranging from 83.5-105.6 ng L⁻¹. HCl extractions released between 58.4-77.4 ng g⁻¹ Cd, and the MC, AO, and CBD extractions released a maximum of 17.71 ng g⁻¹ Cd.

3.2.3 Soil Carbon Emissions

Greenhouse gas emission data in Figures 3 and 4 vary with Fe and Mn treatments and concentrations. The data in Figure 3a, the Fe treatments, show CH₄ emissions increased over time, and with concentration of Fe added. In Figure 3b, where Mn was added, these data show CH₄ production is lower than when Fe is added, with the lowest CH₄ produced in the 1% additions. The 1% Mn amendment sample CH₄ total emissions are constant throughout each sampling date of the experiment, while the 3% and 5% Mn amendment samples increased CH₄ emissions throughout the experiment. In Figure 3c, the Fe and Mn treatments, CH₄ levels are consistent throughout the 56 days, suggesting that either

almost all the CH₄ was produced in the first 4 days. The data also show lower CH₄ emissions with lower Fe/Mn amendment concentrations added to samples.

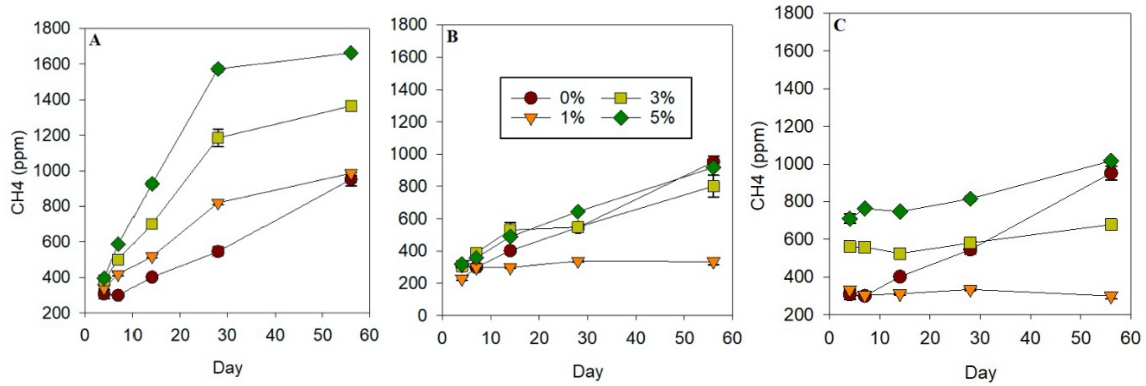


Figure 3: Anaerobic experiment CH₄ emissions from magnetite treatment (A), MnO₂ treatment (B), and magnetite and MnO₂ treatment (C). Error bars represent standard error of experimental triplicates.

The Fe treatments produced CO₂ concentrations greater than the 0-treatment sample over the first 28 days, then significantly less than the 0-treatment sample on day 56 due to a huge spike (Figure 4). Concentration of the Fe amendment did not have an observed impact on CO₂ production. The data in Figure 4b, the MnO₂ nanoparticle amendment, the data show CO₂ production was 0 across all days and concentrations except the 0% sample. The data in Figure 4c, the Fe/Mn amendment samples, we see very small amounts of CO₂ produced, all below 2,000 ppm, except the 0% sample, that slightly increase with time, and are highest in the 1% treatments.

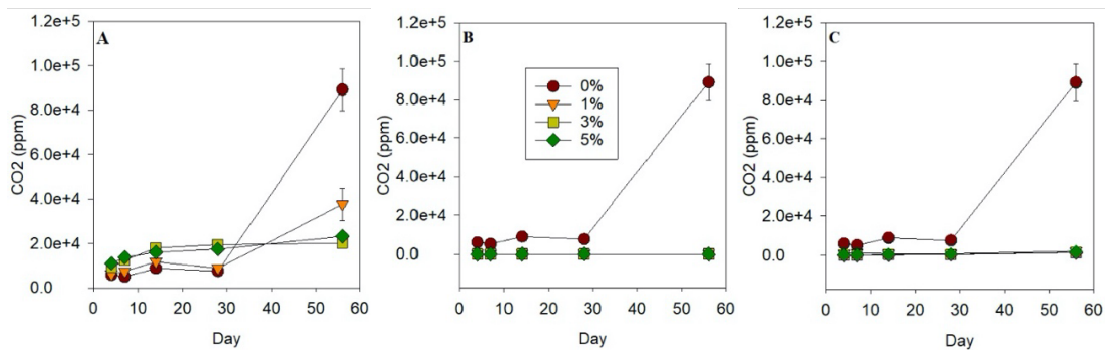
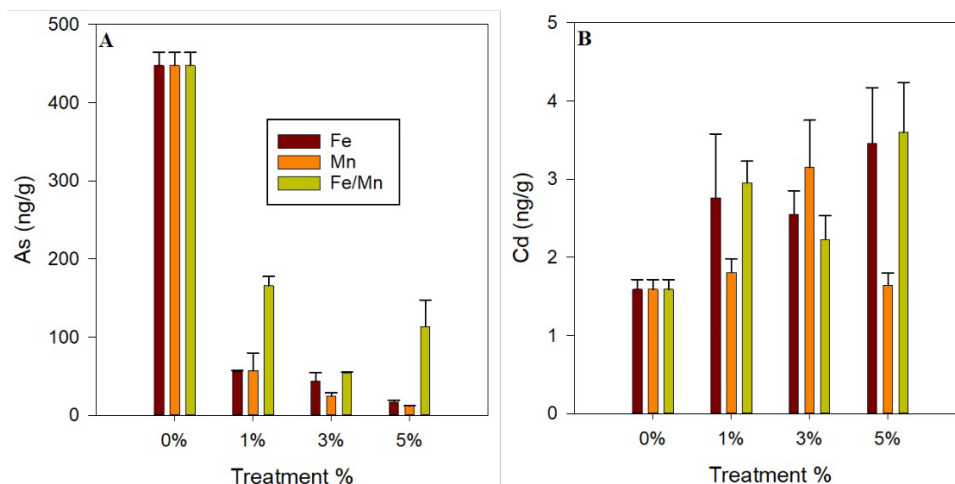


Figure 4: Anaerobic experiment CO₂ emissions from magnetite treatment (A), MnO₂ treatment (B), and magnetite and MnO₂ treatment (C). Error bars represent standard error of experimental triplicates.

3.2.4 Comparing Treatments

The nanoparticle magnetite and MnO₂ amendments decreased As concentrations, increased Cd concentrations, decreased CO₂ emissions and CH₄ emissions were increased and decreased depending on treatment and concentration. These data in Figure 5a show As concentrations of samples treated with Fe or Mn significantly lower than the no treatment sample. While As concentration decreased, data in Figure 5b show that Cd concentration increased in about every sample with the exceptions of the 1% and 5% Mn treatments where they were about the same as the treatment blank. Magnetite treatments increased CH₄ emissions, with the 5% amendment increasing CH₄ production the most and the 1% and no treatment samples producing the least. For the samples with Mn added (including Fe/Mn), the 5% treatment was similar to the no treatment, but in the 3 and 1% treatment samples were lower than the no treatment. The 1% Fe and Fe/Mn treatments had the least CH₄ produced by a decent amount. In Figure 5d, CO₂ week 8 data, all samples were much lower than the no treatment, given a huge spike in CO₂ produced in the 8 week no treatment samples. There was CO₂ produced in all the magnetite treatments, there was no CO₂ produced in the MnO₂ samples, and very small concentrations of CH₄ produced for the Fe/Mn data for the week 8 samples.



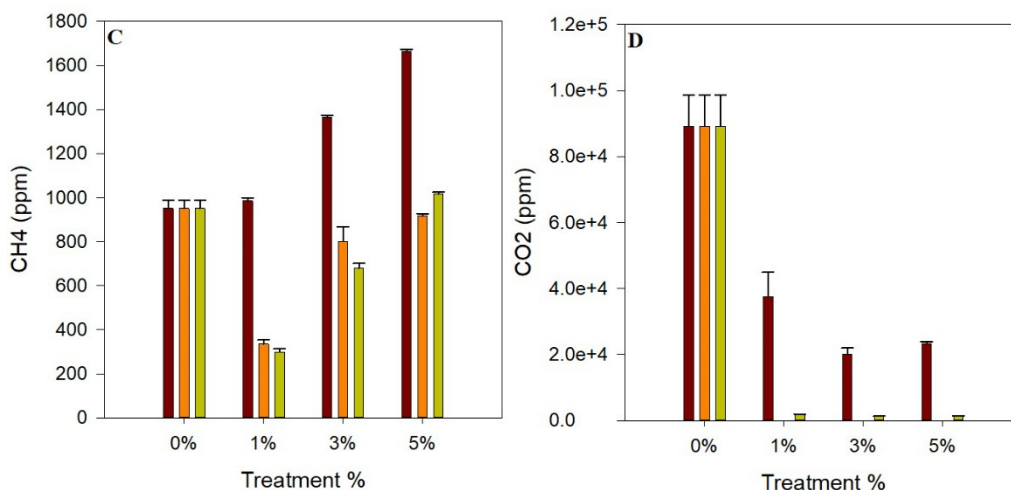


Figure 5: Week 8 anaerobic experiment data compared across treatments for As (A), Cd (B) released into solution and CO₂ (C), and CH₄ (D) emissions from the soil. Error bars represent standard error of experimental triplicates.

3.3 Experiment 2: Aerobic Study

In our follow up aerobic incubation experiment, As concentrations were low through all treatments, magnetite increased Cd concentrations, and MnO₂ decreased Cd released (Figure 6).

As concentrations in solution throughout the study ranged from 0.2-0.7 ng g⁻¹. Cd concentrations in solution were low through the first 14 days of the study, and then spike at 28 days. All of our Cd results are significantly higher than the anaerobic study, which had a spike at 28 days, but MnO₂ treated samples reduced Cd concentrations relative to the magnetite and no treatment samples.

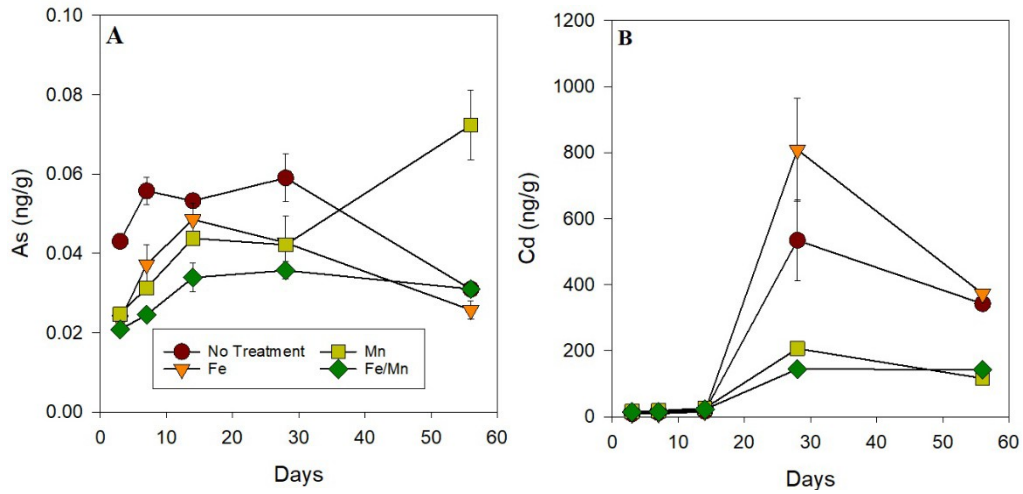


Figure 6: Aerobic experiment As released (**A**), Cd released (**B**) from soils with each treatment. Error bars represent standard error of experimental triplicates.

IV. DISCUSSION

4.1 Anaerobic Study

Soils treated with nanoparticle magnetite amendment had little As released into solutions, with minimal impacts on Cd dynamics. However, depending on amendment concentration, it can increase CH₄ emissions. In the 1% Fe sample, we see methane emissions similar to that of the no treatment, so lower concentration amendments of magnetite have the potential of sequestering As in reduced environments while having little impact on cadmium mobility and possible CH₄ production.

Nanoparticle MnO₂ amendments reduced As concentration in solution without mobilizing Cd, reduced CH₄ production, and inhibited CO₂ production. Arsenic readily binds to Fe-oxides, which Mn-oxides can oxidize if reduced (23). This can explain how we measured no Fe in solution in samples treated with Mn, and low As concentrations in solution. Mn also reduced the amount of CH₄ produced for the 1% amendment and was similar emissions in all the other concentrations (Figure 3). For this treatment there was no CO₂ produced throughout the entire experiment (Figure 4), suggesting that Mn could be toxic at treatment concentrations to certain microbes (24). Lower concentrations of Mn should be studied to see impacts of smaller amendments on GHG emissions and contaminant mobility in paddy soils.

In dually treated samples that received nanoparticle magnetite and MnO₂ amendments, As and CH₄ concentrations were reduced (Figures 1 and 3) relative to no treatment samples, while minimally impacting Cd relative to the oxic study (Figures 2 and 6b), and limiting CO₂ production (Figure 4). The 1% amendment had the lowest CH₄ emissions out of all samples over 56 days, and had similar results for As and Cd release as the 3% and 5% treatment concentrations. Limiting the treatment concentration while decreasing As and Cd released, and CH₄ production is optimal for a solution. Further research into lower and varying concentrations of these amendments can optimize this strategy.

4.2 Oxic Study

In the oxic incubation, Cd concentrations increased by over an order of magnitude under all treatments relative to the anaerobic incubation, and the magnetite amendment increased [Cd] to levels higher than the samples that did not receive an amendment.

There is a spike in cadmium that occurred between 2 and 4 weeks into the incubation, so oxidizing a field with this treatment for harvest might not result in cadmium uptake by rice, though this needs further investigating. Also, only one treatment concentration was used in the oxic study, so further investigation needs to be done on the concentration of Mn amendments to paddy soil and their impact on Cd.

4.3 Future Challenges

Growing rice in the future faces a multitude of challenges, many related to environmental quality, and we need solutions ready to address these challenges to ensure we have a well-nourished global population. Managing rice paddy fields to address contaminant fate, water scarcity, climate change, and rice yields are a hard task to achieve simultaneously (25, 26). Results from our study indicate that using MnO₂ amendments to alleviate the cadmium contamination from AWD irrigation practices can reduce Cd mobility, however none of our amendments demonstrated that they can reduce Cd concentrations in that environment.

In our study, all treatments in the anaerobic incubation demonstrated that they can address some of the challenges presented to rice growing, though more research is needed to investigate the possible externalities from these amendments. Future research needs to look into the use of Fe and Mn nanoparticles applied to paddy soil at smaller amendment concentrations to investigate if we see similar results. We recommend these amendments are tested on field studies with flooded irrigation to see if what we observe in the laboratory translates to the field. We advocate for the use of magnetite at low concentrations in flooded systems to alleviate As contamination, and MnO₂ for lowering soil emissions, however, there needs to be more research into the implications of varying

the amendment concentration. By addressing these questions, we will be able to improve the quality of rice without decreasing yield and limiting negative impacts from this practice.

Overall a combination of Fe and Mn seems like it could be ideal at addressing this issue, as you can gain benefits from them both in different ways. The 1% Fe treatment seems like it is ideal for an anaerobic system, but it does not reduce CH₄, and Cd can still be mobilized upon oxidation of the field. The 1% Mn seems like too large of a concentration to pair with the Fe, as it impacts microbes more and results in high Mn in solution, therefore, further investigations into Mn amendments at lower concentrations, paired with Fe seem like the ideal way to address the issue. Honing in on ideal concentration for the amendments can prevent rice from taking up As and Cd as well as lower CH₄ emissions.

V. CONCLUSION

Global rice contamination by As and Cd is a well-documented challenge with no known solutions that address both contaminants. The driving factors that cause the contaminations are tied to irrigation practices that influence redox processes and contaminant sorption in paddy soils. Our results demonstrate that nanoparticle magnetite can be used to sorb As in reduced environments, while not mobilizing Cd, though you risk increasing CH₄ emissions. They also demonstrate that in an oxic environment, nanoparticle MnO₂ can reduce Cd availability. Both amendments had varying influence on CH₄ and CO₂ emissions so future research needs to elucidate the impacts of these amendments on emissions in a field study. Solutions to address these challenges are critical and many parts of the world are relying on them for growing rice in a safe matter.

REFERENCES CITED

- 1) Importance of rice - RICE: CGIAR Research Program on Rice Agri-Food Systems. (n.d.). Retrieved July/August, 2020, from <http://ricecrp.org/importance-of-rice/>
- 2) Yamaji, Naoki, Mitani, Namiki, Xu, Xiao-Yan, Su, Yu-Hong, Ma, J F, Yamaji, N, Mitani, N, Xu, X-Y, Su, Y-H, McGrath, S P, and Zhao, F-J. "Transporters of Arsenite in Rice and Their Role in Arsenic Accumulation in Rice Grain." *Proceedings of the National Academy of Sciences of the United States of America*. 105.29 (2008): 9931-935. Web.
- 3) Meharg A. A.; Rahman M. Arsenic contamination of Bangladesh paddy field soils: Implications for rice contribution to arsenic consumption. *Environ. Sci. Technol.* 2003, 37, 229-234.
- 4) Chang, Jiali, Liu, Pengfei, Fu, Li, Ding, Dwen, Li, Huijuan, and Lu, Yahai. "Direct Interspecies Electron Transfer Accelerates Syntrophic Oxidation of Butyrate in Paddy Soil Enrichments." *Environmental Microbiology*. 17.5 (2015): 1533-547. Web.
- 5) Wang, Ping-Mei, Gu, Yi, Kopittke, Peter M., Zhao, Fang-Jie, Wang, Jing, Kopittke, Peter M, and Wang, Peng. "Iron–Manganese (Oxyhydro)oxides, Rather than Oxidation of Sulfides, Determine Mobilization of Cd during Soil Drainage in Paddy Soil Systems." *Environmental Science & Technology*. 53.5 (2019): 2500-508. Web.
- 6) Lundy, Mark E., Linquist, Bruce A., Carrijo, Daniela R, Lundy, Mark E, and Linquist, Bruce A. "Rice Yields and Water Use under Alternate Wetting and Drying Irrigation: A Meta-analysis." *Field Crops Research* 203 (2017): 173-80. Web.
- 7) Arao, Tomohito, Kawasaki, Akira, Baba, Koji, Mori, Shinsuke, and Matsumoto, Shingo. "Effects of Water Management on Cadmium and Arsenic Accumulation and Dimethylarsinic Acid Concentrations in Japanese Rice." *Environmental Science & Technology*. 43.24 (2009): 9361-367. Web.
- 8) LAGOMARSINO, Alessandra, AGNELLI, Alessandro Elio, LINQUIST, Bruce, ADVIENTO-BORBE, Maria Arlene, AGNELLI, Alberto, GAVINA, Giacomo, RAVAGLIA, Stefano, and FERRARA, Rossana Monica. "Alternate Wetting and Drying of Rice Reduced CH₄ Emissions but Triggered N₂O Peaks in a Clayey Soil of Central Italy." *Pedosphere*. 26.4 (2016): 533-48. Web.
- 9) Carrijo, D.R., Lundy, M.E., Linquist, B.A., 2017. Rice yields and water use under alternate wetting and drying irrigation: a meta-analysis. *Field Crop Res.* 203, 173–180.

- 10) Seyfferth, A. L., Limmer, M. A., & Dykes, G. E. (2018). On the Use of Silicon as an Agronomic Mitigation Strategy to Decrease Arsenic Uptake by Rice. *Advances in Agronomy*, 49–91.
- 11) Amaral, Douglas, Limmer, Matt A., Guilherme, Luiz R. G., Seyfferth, Angelia L, Limmer, Matt A, and Guilherme, Luiz RG. "Combined Impacts of Si-rich Rice Residues and Flooding Extent on Grain As and Cd in Rice." *Environment International* 128 (2019): 301-09. Web.
- 12) Penido, E.S., Bennett, A.J., Hanson, T.E. et al. Biogeochemical impacts of silicon-rich rice residue incorporation into flooded soils: Implications for rice nutrition and cycling of arsenic. *Plant Soil* 399, 75–87 (2016). <https://doi.org/10.1007/s11104-015-2682-3>
- 13) Wang, Xin, Peng, Bo, Tan, Changyin, Ma, Lena Q., Yin, Daixia, and Ma, Lena Q. "Effect of Biochar and Fe-biochar on Cd and As Mobility and Transfer in Soil-rice System." *Chemosphere*. 186 (2017): 928-37. Web.
- 14) Chen, Zheng, Cai, Chao, Tie, Baiqing, Liu, Xiaoli, Zheng, Ruilun, Reid, Brian J, Huang, Qing, Lei, Ming, Sun, Guoxin, and Baltrėnaitė, Edita. "Mitigating Heavy Metal Accumulation into Rice (*Oryza Sativa* L.) Using Biochar Amendment — a Field Experiment in Hunan, China." *Environmental Science and Pollution Research International* 22.14 (2015): 11097-1108. Web.
- 15) Xin Xiao, Baoliang Chen, and Lizhong Zhu. Transformation, Morphology, and Dissolution of Silicon and Carbon in Rice Straw-Derived Biochars under Different Pyrolytic Temperatures *Environmental Science & Technology* 2014 48 (6), 3411-3419 DOI: 10.1021/es405676h
- 16) Borch, T., Kretzschmar, R., Kappler, A., Cappellen, P. Van, Ginder-Vogel, M., ... Voegelin, A. (2010). Biogeochemical Redox Processes and their Impact on Contaminant Dynamics. *Environmental Science & Technology*, 44(1), 15–23. <https://doi.org/10.1021/es9026248>
- 17) Chowdhury SR, Yanful EK. Kinetics of cadmium(II) uptake by mixed maghemite-magnetite nanoparticles. *Journal of Environmental Management*. 2013 Nov;129:642-651. DOI: 10.1016/j.jenvman.2013.08.028.
- 18) Makino, Tomoyuki, and Suda, Aomi. "Functional Effects of Manganese and Iron Oxides on the Dynamics of Trace Elements in Soils with a Special Focus on Arsenic and Cadmium: A Review." *Geoderma*. 270 (2016): 68-75. Web.
- 19) Huber DL. Synthesis, properties, and applications of iron nanoparticles. *Small*. 2005 May;1(5):482-501. doi: 10.1002/sml.200500006. PMID: 17193474.

- 20) Sun J, et al. Enhanced and Stabilized Arsenic Retention in Microcosms through the Microbial Oxidation of Ferrous Iron by Nitrate. *Chemosphere*. 2016;144:1106–1115.
- 21) Li, B., Zhou, S., Wei, D., Long, J., Peng, L., Tie, B., ... Lei, M. (2019). Mitigating arsenic accumulation in rice (*Oryza sativa* L.) from typical arsenic contaminated paddy soil of southern China using nanostructured α -MnO₂: Pot experiment and field application. *Science of the Total Environment*, 650, 546–556. <https://doi.org/10.1016/j.scitotenv.2018.08.436>
- 22) Gillispie, E. C., Andujar, E., & Polizzotto, M. L. (2016). Chemical controls on abiotic and biotic release of geogenic arsenic from Pleistocene aquifer sediments to groundwater. *Environ. Sci.: Processes Impacts*, 18(8), 1090–1103. <https://doi.org/10.1039/C6EM00359A>
- 23) Dixit, S., & Hering, J. G. (2003). Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. *Environmental Science & Technology*, 37(18), 4182–4189. <https://doi.org/10.1021/es030309t>
- 24) Cheung, H. Y., Vitkovič, L., & Brown, M. R. W. (1982). Toxic Effect of Manganese on Growth and Sporulation of *Bacillus stearothermophilus*. *Microbiology*, 128(10), 2395–2402. <https://doi.org/https://doi.org/10.1099/00221287-128-10-2395>
- 25) Shi, Z., Carey, M., Meharg, C. et al. Rice Grain Cadmium Concentrations in the Global Supply-Chain. *Expo Health* (2020). <https://doi.org/10.1007/s12403-020-00349-6>
- 26) Peng, S., Huang, J., Sheehy, J. E., Laza, R. C., Visperas, R. M., Zhong, X., ... Cassman, K. G. (2004). Rice yields decline with higher night temperature from global warming. *Proceedings of the National Academy of Sciences*, 101(27), 9971–9975. <https://doi.org/10.1073/pnas.0403720101>
- 27) EPA (1996) Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. Revision 2.
- 28) N. Keon, C. Swartz, D. Brabander, C. Harvey, H. Hemond Validation of an arsenic sequential extraction method for evaluating mobility in sediments *Environ. Sci. Technol.*, 35 (2001), pp. 2778-2784

- 29) O.P. Mehra, M.L. Jackson Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate Clays and Clay Miner. Proc. Seventh Nat.Conf. (1960), pp. 317-327