USING IRIS FILMS TO
INFORM ALTERNATE WETTING
AND DRYING (AWD) WATER
MANAGEMENT IN RICE PADDIES

by

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DEDICATION

This work is dedicated to my amazing parents Richard and Karen Evans who taught me to work hard and never give up on my dreams. I wouldn’t be who I am today without your love and support. To my loving sisters, Alyssa Evans and Emily Hall who inspired me to be a better person. To my friends who encouraged me every step of the way, and to my best friend and fiancé, Michael Reeves. Graduate school would have been much less interesting without you. Thank you for going to the rice paddies with me at 2am to pull IRIS films and always keeping me motivated to push through all the hard days.
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ABSTRACT

Rice is a crucial part of the world’s food supply as over half of the world’s population eats it daily. Many rice farmers depend on rice production for their livelihoods; however, they face a difficult task of how to minimize contaminant uptake while maintaining yield. Rice is generally grown in flooded soil conditions, under which arsenic becomes more plant available. Arsenic is naturally found in the soil and when taken up by the rice plant it can decrease yield and grain quality. Arsenic’s impact on rice can be alleviated by increasing the soil redox potential, but this could increase cadmium plant-availability. Careful control of soil redox by implementing alternate wetting and drying (AWD) of the soil can decrease concentrations of plant-available arsenic and cadmium in the soil, but farmers in developing countries need a way to easily monitor soil redox. Indicator of Reduction in Soil (IRIS) tubes and films have been studied in recent years as a method of measuring soil redox potential in wetland environments. My work explores the use of the IRIS film technology as indicators of soil redox in rice fields as a low-tech means to indicate when farmers should drain their fields to minimize contaminant uptake. This study took advantage of an ongoing rice mesocosm study at the University of Delaware, where 30 rice paddies under different management have been instrumented with porewater samplers and continuous redox probes. Indicator of Redox in Soil (IRIS) films coated with Fe or Mn
oxides were prepared and deployed in 6 different rice paddies initially after rice paddies were allowed to dry to > 30 cm below the soil surface (severe AWD) and again when paddies were only allowed to dry to 15 cm below the soil surface (safe AWD). The goal of this study was to test the response time of IRIS films to various conditions of soil redox and to establish the IRIS films as a tool for monitoring AWD in rice paddies. I explore quantification methods of paint loss from films, optimal residence time of films in situ, IRIS film paint removal as it relates to porewater chemistry and redox measurements, and highlight important considerations for the use of IRIS films to monitor AWD worldwide.
Chapter 1
MOTIVATION AND LITERATURE REVIEW

Arsenic is a naturally-occurring metalloid in the environment but is not essential for life\textsuperscript{1,2} While many forms of arsenic (As) can be harmful to humans, As in its inorganic form is especially toxic and is classified as a Class I human carcinogen\textsuperscript{3}.

Prolonged or chronic exposure to inorganic As can have serious health implications including, but not limited to skin, liver, kidney and cardiovascular diseases as well as gastrointestinal issues and cancer\textsuperscript{3,4}. Most As intake by humans is via consumption of contaminated water and food, especially in regions where groundwater As levels are elevated, such as Bangladesh and India\textsuperscript{5,6}. An especially problematic crop for As contamination is rice because it is a staple food for much of the world and its growing conditions make As more available for plant uptake. Because of this, As poses a serious threat to food security and human health\textsuperscript{7}.

Arsenic in the Environment

Arsenic concentrations vary widely in the environment, mostly depending on mineral content and composition of soil and parent material\textsuperscript{6}. While the earth’s upper crust contains only 2 mg/kg of elemental As\textsuperscript{8}, natural levels in soils generally range from 1-50 mg/kg with an average of 5 mg/kg\textsuperscript{9}. However, much higher levels can occur in
contaminated areas such as mining sites, areas surrounding coal smelters, and near large deposits of As rich minerals\textsuperscript{9}.

Soil and rock concentrations of As greatly influence As availability in water. Concentrations of As in surface and groundwater varies greatly depending on the surrounding environment and factors including erosion, chemical composition of soil and rock formations, and geothermal hotspots. Concentrations of available As in groundwater tend to be higher than in surface water due to reducing conditions and water-rock interactions in groundwater\textsuperscript{6,7,10}. An overwhelming majority of natural waters, such as lakes, rivers and groundwater in the United States and around the world have As concentrations between 0.2 - 10 μg/L, over half of which are less than 1 μg/L\textsuperscript{11}. However, areas of contamination, such as areas near mine tailings or aquifers containing naturally As rich rock, can lead to much higher As levels in natural waters. Groundwater As levels in the United States and Canada are very diverse across the landscape; areas of California and Nevada have recorded As levels as high as 2,600 μg/L and aquifers near mine tailings in Alaska, and Canada have recorded As concentrations that are higher than 5,000 μg/L\textsuperscript{6,12,13}. Additionally, many Asian countries like Bangladesh, and India have areas with naturally elevated groundwater As. Ranges of groundwater As in Bangladesh are between <10 and 2,500 μg/L, with potential exposed population of as many as 30 million\textsuperscript{6,14}. Similarly, groundwater As concentrations in West Bangel India can range from <10 to 3,200, with a potential exposed population as high as 6 million\textsuperscript{6,15}. Groundwater concentrations of As in Argentina have been recorded over 5,000 μg/L\textsuperscript{6,16}. 
These higher levels of As in natural waters are especially problematic if that water is used as a drinking water source. The World Health Organization’s (WHO) drinking water concentration guideline for As is 10 μg/L\textsuperscript{17}. However, many individual countries (mostly developing nations) have a higher drinking water As limit, some up to 50 μg/L, mostly in developing nations\textsuperscript{6}, because it is prohibitively expensive to decrease As to concentrations lower than 50 μg/L. Occurrences of As contamination in drinking water is variable around the world and within individual countries due to the diversity of hydrogeology of different regions. Many areas of high As in groundwater have been reported in the United States including New Hampshire, where one study reported that 10% of household wells contain >10 μg/L\textsuperscript{10}. Hotspots of As in groundwater also exist in the Southwest United States (i.e., California, Nevada, and Arizona), where some counties show As concentrations >10 μg/L in at least 25 percent of the groundwater sampled\textsuperscript{18}.

Similarly, across the world in Bangladesh and West Bengal, India, high levels of As in drinking water can be found in areas were As contamination is extremely prevalent in groundwater. Bangladesh is a particularly notorious example of high drinking water As levels\textsuperscript{19,20}. In the 1970’s, aid organizations like The United Nations Childrens Fund (UNICEF) worked diligently to install shallow tube wells across Bangladesh\textsuperscript{20}. At the time, drinking water was typically taken from surface waters, resulting in bacterial infections and caused many gastrointestinal diseases in children; so it was believed that tube wells would provide a cleaner and safer source of water to the people of Bangladesh\textsuperscript{21}. What UNICEF did not know was that the groundwater was naturally contaminated with As. As such, installation of tube wells only created a more toxic
situation for the people drinking from the wells\textsuperscript{21}. Still, the people Bangladesh and are just a portion of the estimated 160 million people living in areas of naturally elevated As in drinking water\textsuperscript{21}.

The public health crisis brought on by the installation of tube wells in Bangladesh prompted many studies on the human health risk of As in drinking water. One study done in Bangladesh revealed As concentrations in drinking water as high as 2,040 μg/L\textsuperscript{22}. Another study in India found that drinking water As concentrations were typically <500 μg/L, but concentrations as high as 3,400 μg/L were recorded\textsuperscript{23}. Both studies were concerned with the prevalence of skin lesions on people who were drinking contaminated water; the researchers found that people who consumed water with larger amounts of As over time had a higher occurrence of skin lesions than those that did not have quite as much exposure. Surprisingly though, both studies found that people drinking water with relatively low As concentrations still had a high prevalence of As-associated skin lesions. Based on these results, the researchers suggested that while As in drinking water is considered the main source of human inorganic As intake,\textsuperscript{24} eliminating As in drinking water through expensive remediation or changing the source of drinking water would not completely eliminate the threat of As due to the consumption of contaminated food\textsuperscript{7}.

\textit{Arsenic in Food}

Arsenic in food poses a serious threat to food security and human health\textsuperscript{7}. Food can become contaminated in a couple of different ways. One is through physical adhesion of contaminated soil particles to the surface of vegetables like leafy greens such as lettuce, spinach, and kale as well as broccoli and cabbage\textsuperscript{25}. Another food contamination
mechanism is plant uptake of As through plant root systems. When soil is contaminated with high levels of As, that As can become mobile and available for plant uptake. While some soils have natural As concentrations, irrigating crops with As contaminated water also leads to extremely high levels of As in soil and porewater. Some plants are capable of taking up and storing As in the part of the plant that we consume, one of which is rice.

*Arsenic in Rice*

Rice is a staple crop for a large portion of the world and its production in typical flooded growing conditions make As more mobile and available in the soil. A study in India revealed that the As in groundwater used to cultivate rice and vegetables was very high, ranging from 103 - 827 μg/L and resulted in an average level of 0.323 μg/g of As in rice, with a range of 0.120 μg/g - 0.663 μg/g. Typical concentrations of As in rice are different depending on the type of rice and where it is produced, but ranges from 0.057 - 0.191 μg/g as reported by the Food and Drug Administration (FDA). The CODEX value, which is an international food standard regulation, is 0.35 μg/g of As for brown rice and 0.20 μg/g for polished white rice. While the average level of As in rice for the previously mentioned study in India was compliant with CODEX standards, many people were consuming rice well above (and even almost double) the international food standard. Because rice is a staple crop in India, the researchers reported that many people eat mostly rice and vegetables for every meal, which leads to a daily intake of about 100 μg of As just from food. This number could be higher or lower depending on dietary habits, age, and weight of the consumer and the level of contamination in the
food. Additionally, studies have shown that As in rice tends to be in the more toxic inorganic form compared to other food sources like seafood, which mainly contain less toxic organic As forms\textsuperscript{29,32}. Because of this, As in rice is considered a human health concern and has been widely studied.

While As in rice grain poses a threat to human health, it can also effect grain yield, which can lead to economic stress and further lack of food security for rice farmers and their families in effected areas\textsuperscript{33,34}. Arsenic accumulation in rice plants can cause a decrease in above ground biomass, chlorosis, or lack of grain fill and therefore, significantly reduced grain yield\textsuperscript{35,36}. Reduced yield puts stress on farmers and communities. In order for a community to be food secure, all people at all times must have physical, social, and economic access to safe food that is healthy and supplies sufficient nutrients that they need to live a healthy life\textsuperscript{37}. In countries where people eat rice for every meal, their food security and their health are at risk due to As in their soil and water.

**Arsenic Mobility in Soils**

*Reductive Dissolution*

Rice is an especially unique crop because rice is grown in flooded soils, which can increase As mobility in soil and porewater due to microbially-mediated reductive dissolution of As-bearing metal oxides\textsuperscript{38}. When soil is oxidized, As(V) can sorb to the surface of Fe(III) and Mn(III/V) oxy(hydr)oxide minerals, as well as other minerals such as aluminum hydroxides and aluminosilicate clays\textsuperscript{39,40}. However, when soil is flooded, as
it generally is in rice production, the soil becomes suboxic and anoxic. This lack of oxygen suppresses metabolisms of strictly aerobic microorganisms, and anaerobic microorganisms can compete for carbon compounds while using alternate electron acceptors for carbon oxidation according to a progression referred to as the redox ladder (Figure 1.1). While oxygen is the most energetically-favorable electron acceptor for aerobic organisms, anaerobic organisms can utilize other compounds, with each yielding less energy for the organism in the following order: nitrate, manganese (III/V), iron (III), sulfate, and oxidized carbon (CO$_2$). In soils, Fe (III) and Mn (III/V) are major sorbents for As; Fe(III) is known to be abundant in many soil types. Because of this, reductive dissolution of Fe and Mn minerals plays a major role in the release of As(V) to soil solution (Figure 1.2). Once As(V) is released from Fe and Mn oxy(hydr)oxide minerals, microorganisms can reduce it to As(III), which is more mobile and available for plant uptake. At this point of As release to porewater, Mn oxides play an important role in the oxidation of As(III). It is important to note that because of the heterogeneity of soil microenvironments, the order of reduction of the alternate electron acceptors on the redox ladder does not always follow the typical progression. Reduction of each component depends on the redox state of the soil and the microbial community composition, as well as the relative concentrations of electron acceptors.
Figure 1.1: The redox ladder depicts how the lack of oxygen under suboxic and anoxic conditions in soil leads to the reduction of different soil compounds by anaerobic microorganisms. The black text on the top of each stair step represent the oxidized component, while the white text under each stair step represents the corresponding reduced component. The bold text to the right of each step is the active microbial community for the reduction of the corresponding compound(s). Mn and Fe reducers are in red because they are most important to the release of As in soil.

Figure 1.2: Reductive dissolution of Fe oxide minerals results in release of As to the soil porewater. While the reductive dissolution of Mn oxide minerals can also release As to the soil porewater, Mn oxides have the ability to oxidize Fe(II) to Fe(III) and As(III) to As(V), which is important because it allows for the resorption of As(V) to mineral surfaces.
The Unique Role of Manganese

In addition to reductive dissolution, some Mn oxides like layered Mn-oxide minerals (phyllomanganates), have the ability to oxidize As(III) species to As(V), which then sorbs to mineral surfaces\(^45\) (Figure 1.2). This process of As(III) oxidation followed by sorption has been shown to create a higher level of As sorption than with that of As(V) species that were not oxidized by the phyllomanganate\(^45,46\). Lafferty\(^47\) found that As that had been oxidized and sorbed to Mn did not fully desorb under various conditions\(^47\). These results could mean that when phyllomanganates are present in the soil, they could tie up some As in the soil despite reductive dissolution. Even so, numerous studies have concluded that while reduction of Mn oxides does release As in to porewater, As most likely rapidly resorbs to Fe oxides. Therefore, it is the reduction of Fe oxides that truly drives the release of As in to porewater\(^48,49\). Once the As(V) released from reductive dissolution of Fe and Mn oxides is free in soil solution, it is available for transformation and methylation. It has been shown that under reducing conditions, As(V) is reduced to the more mobile and toxic form As(III)\(^42–44\), which is either methylated or available for plant-uptake. Both methylated As and As(III) are taken up by rice plants and accumulated in plant tissue and rice grain where it can impact food security.
**Water Management to Decrease Arsenic Uptake in Rice Plants**

While soil amendments and genetic approaches\textsuperscript{50–53} have been found to decrease As uptake by rice, water management is the strategy most widely practiced by rice farmers (both in developed and developing countries) with varying levels of success. The obvious solution to decrease grain As accumulation is to grow rice in non-flooded conditions to limit As mobility. However, rice production under non-flooded conditions this is not a viable solution because without the proper use of expensive herbicides, weeds can overtake a non-flooded rice field, in some cases decimating the crop yield\textsuperscript{54,55}. Weeds alone have been estimated to account for 35\% of worldwide potential rice yield loss\textsuperscript{54}. Flooded rice is highly desirable in terms of weed management and has been shown to produce higher yields than non-flooded rice\textsuperscript{56}. Additionally, while growing rice in non-flooded soils does decrease As mobility and, therefore, plant uptake in rice plants, it has been shown to increase plant cadmium (Cd) concentrations\textsuperscript{56,57}. Like As, Cd is toxic to humans and can accumulate in rice grain\textsuperscript{58}. Cadmium is also naturally occurring and contaminates many of the same areas as As\textsuperscript{57,58}. Unlike As, Cd is more readily available for plant uptake when soil is oxidized. Under reducing conditions Cd is bound to sulfur in the form of cadmium sulfide (CdS). When soil is aerobic, sulfide is oxidized to sulfate (SO$_4^{2-}$) and Cd is solubilized and available for plant uptake\textsuperscript{59,60}. It is this tradeoff between As and Cd mobility that poises alternate wetting and drying (AWD) as an effective water management practice to decrease both As and Cd uptake in rice plants.
Alternate Wetting and Drying (AWD)

Unlike conventional flooded rice production, AWD is a management strategy in which soils are periodically drained and reflooded during the rice growing season. This allows soil to become aerobic for a period of time before reflooding, which can simultaneously limit both As and Cd mobility in the soil. As previously described, when soil is aerobic, As can sorb to Fe and Mn oxy(hydr)oxide minerals, but when flooded, As is released due to reductive dissolution (Figure 1.3). AWD allows the soil to be flooded when it is most imperative for plant growth during stages like flowering and grain fill in order to maintain yield, but creates conditions that favor Fe and Mn oxide precipitation and subsequent As sorption when soil is periodically allowed to become aerobic. Moreover, production of rice with AWD also decreases water use and methane emissions. This is beneficial because rice production is one of the largest uses of agricultural water and accounts for about 11% of non-CO₂ greenhouse gas emissions from agriculture worldwide.

Alternate wetting and drying management does not require expensive equipment and is relatively easy for farmers to implement under the right social and environmental conditions. For instance, adoption of AWD requires that the farmer have irrigation infrastructure, economic access to irrigation water, and control of irrigation practices, which is not always the case in developing nations especially for sharecroppers or farmers participating in community supported agriculture. Additionally, AWD is extremely dependent on weather conditions during dry cycles, which is why adoption of AWD is limited in rainfed rice systems or in areas with little to no irrigation or water
management infrastructure, as farmers fear the lack of water availability when fields need to be reflooded\textsuperscript{67}.

Farmers who are able and want to implement AWD must install a perforated water measurement well that can be made out of perforated PVC pipe, bamboo, or any other rigid cylindrical material that measures at least 40 cm long and 10-15 cm in diameter\textsuperscript{63}. Installation of the water measurement well is recommended in an easily accessible place in the rice field that is representative of the average water depth in that field\textsuperscript{63}. Multiple wells could be installed into the same field, especially if the field is of considerable size. The well should be installed so that at least half of its length is in the ground leaving around 15 cm above the soil surface (Figure 1.4). The process of AWD can begin approximately one week after transplanting or when plants are 10 cm tall when direct seeding. Implementing AWD is simple and only requires that the farmer does not flood their field until the water level in the well reaches 15 cm below the soil surface. If multiple wells are being utilized, an average depth of 15 cm is used to signal reflooding. When reflooding, farmers can again use the well to reflood to 5 cm above the soil surface\textsuperscript{63}. This AWD strategy is often referred to as “safe AWD” because it has been shown to reduce water use without an impact on rice yield, so it is a “safe” option for farmers\textsuperscript{69}. Some variations of AWD have been studied to test the effectiveness of more severe AWD timing strategies, specifically on decreasing As content in rice grain without compromising rice yield.
Figure 1.3: Non-flooded or oxic conditions promote sorption of As to Fe and Mn oxides, however Cd is readily available. Flooded or anoxic conditions ties up Cd but releases As through reductive dissolution. AWD is an alternation of both conditions.

Figure 1.4: Farmers use water measurement wells to manage AWD. The water table can easily be measured with a tape measure or meter stick.
Effect of AWD on Rice Yield

Some research has been conducted to test the impact of varying severity of AWD on rice yield. As previously mentioned, in practice, safe AWD is managed by monitoring water levels using a perforated PVC tube. Many studies done on AWD have used this practice to manage safe AWD, but some use soil volumetric water content to measure more severe AWD regimens\textsuperscript{70,71}. Many studies have shown that there is no risk for yield loss when practicing safe AWD\textsuperscript{63,72,73}, but severe AWD (which practices deeper or more severe drying) does have the potential for yield loss\textsuperscript{72,74}. Others have shown success with more severe AWD. Carrijo \textit{et al.}\textsuperscript{71} evaluated multiple AWD severities including AWD, AWD35 and AWD25. In this study, AWD mimicked safe AWD where fields were reflooded when the water table reached 15 cm, while AWD35 and AWD25 mimicked a more severe AWD where fields were reflooded when soil volumetric water content at the depth of 0-15 cm reached 35% and 25%, respectively. The researchers did not report a significant yield decrease due to any of the AWD regimens. They suggest that the lack of yield loss in AWD25 and AWD35 may be because water was available at deeper depths in the soil profile, providing sufficient water for plant development\textsuperscript{71}. Carrijo \textit{et al.}\textsuperscript{71} stressed that the effectiveness of AWD regimens is not universal and understanding that the specific soil type, texture and hydrology of the field in question, along with rooting depth and root distribution all being key factors in determining the AWD regimen that will work for a specific field\textsuperscript{71}.

Timing of AWD is also a consideration that has been studied with contrasting opinions. Some research has shown that there is a potential for a rice yield increase under
moderate AWD (more than safe AWD, but less than severe AWD). While most literature on AWD recommends having rice fields flooded during grain fill, two separate studies practiced AWD during grain fill and found that moderate drying during grain fill drives the plant to use stored carbon, which accelerates grain fill and slightly increases yield\textsuperscript{75,76}. Other studies have found that AWD during either vegetative or reproductive plant stages had no effect or a positive effect on grain yield\textsuperscript{72,77}.

Different rice cultivars that have been genetically modified to be drought resistant or drought tolerant have been studied as viable options for reducing yield loss under severe AWD because of their ability to grow under water stress\textsuperscript{78}. While these cultivars have shown success and are an option of farmers who can afford them, they might not be desirable to a lot of rice farmers in the developing world due to cost and the inability to store and reuse genetically modified seed the next year\textsuperscript{79}. Not being able to store and plant these seeds the next year would cut in to farmers profit margins, which may not be feasible for some farmers\textsuperscript{79}.

*Effect of AWD on Grain As and Cd Concentrations*

Variations in AWD severity have also been studied with the goal of decreasing rice grain As and Cd concentrations. While some variation in the effectiveness of AWD on grain As and Cd concentrations has been reported depending on severity and timing of dry downs, most studies suggest that safe AWD (drying to 15 cm below the soil surface) is not sufficient to decrease As uptake because the soil never becomes aerobic enough to immobilize soil As\textsuperscript{71,80,81}. In a two-year field study, Li *et al.*\textsuperscript{80} studied the effect of three AWD treatments on As and Cd concentrations in rice grain compared to a conventional
flooded treatment. Safe AWD treatments (drying to perched water table 15 cm below the soil surface and reflooding) did not significantly decrease grain As concentrations compared to conventional flooding. Treatments with severe AWD, where the soil was dried to 25% volumetric water content at 15 cm, were effective in decreasing grain As concentrations; however, grain Cd concentrations increased. Additionally, AWD management to 35% volumetric water content at 15 cm, which is considered moderate AWD, was effective in minimizing both grain As and Cd\(^\text{80}\). Similarly, Norton \textit{et. al.}\(^\text{81}\), evaluated safe AWD compared to conventional flooding and found that grain As concentrations were slightly decreased under safe AWD; however, Cd concentrations were increased\(^\text{81}\). These studies suggested that soil factors such as pH and initial contaminant concentrations, as well as timing of dry downs can introduce variation in grain As concentration between soils and should be major considerations when choosing an AWD regimen\(^\text{70,81}\).

\textit{Using Eh to Monitor AWD}

Because reductive dissolution of Fe and Mn oxy(hydr)oxides under suboxic to anoxic conditions increases As mobility and availability to plants, careful control of soil redox potential (Eh) could be a very effective way to monitor AWD across different soils. In a field study testing impacts of varying water management strategies on grain As concentration, Honma \textit{et al.}\(^\text{82}\) found that when soil Eh dropped below \(\approx 100 \text{ mV}\), dissolved As and Fe(II) were elevated in soil porewater\(^\text{82}\). These results agreed with previous work that showed Eh is a master variable for predicting As and Cd mobility in pore water\(^\text{83,84}\). Soil Eh is typically measured using platinum electrodes\(^\text{85}\) either manually
using a volt meter or automatically with a data logger. This equipment for measuring Eh is expensive and may not be an option for farmers in developing countries who may want to use AWD to decrease As uptake in rice. A low-cost tool that rice farmers can use to identify the reducing conditions that lead to As mobility in their soil is critically needed. This research aims to establish indicator of redox in soils (IRIS) films as a tool that farmers could use in place of expensive electrodes to measure and identify reducing conditions in paddy soils.

**Indicator of Redox in Soils (IRIS)**

The IRIS technology was first developed by Dr. Byron Jenkinson at Purdue University originating with the use of 1-inch polyvinylchloride (PVC) pipe that was coated with Fe oxide minerals that were synthesized in the laboratory. Tubes were inserted into the soil, and under reducing conditions, the anaerobic Fe reducing bacteria use the Fe oxide on the tube as an electron acceptor effectively reducing the Fe oxide to Fe(II) and stripping it from the tube. This Fe paint removal from the tube can then be quantified and used as an indication of reducing conditions. The IRIS technology was originally developed as a tool to identify hydric soils, specifically in wetland environments and after the many advancements, IRIS tubes were approved by the National Technical Committee for Hydric Soils (NTCHS) in 2007 as a viable method to identify reducing conditions in soil. Since then many different uses of the technology have been explored, but to our knowledge they have never been used in rice paddies.
**Development of a Durable Fe Oxide Paint**

Before the adoption of IRIS as an approved method to identify hydric soils, Dr. Martin Rabenhorst at the University of Maryland worked for many years on developing the technology. One of his first advancements was achieving an Fe oxide suspension (paint) that was primarily poorly crystalline ferrihydrite but contained 30-40% goethite in order to promote adhesion to PVC tubes. Rabenhorst’s procedure for synthesizing Fe paint followed Jenkinson’s previous work\(^8\), but was modified to promote partial transformation of ferrihydrite to goethite\(^7\). This modification resulted in a durable mixed phase Fe paint that had better adhesion to IRIS tubes\(^7\).

Preparation of IRIS tubes was an additional challenge due to their cylindrical nature. A homemade lathe type device was used to spin the tube as the operator paints on the Fe paint using a foam brush. This ensured a more uniform coating on tubes. Once coated and dry, IRIS tubes could be stored indefinitely without alteration of the Fe oxide minerals. Installing the tubes was easy and quick. A pilot hole could be made using a push probe and the tube was inserted directly in to the hole and left for the desired amount of time\(^9\).

**Development of Mn Oxide Paint**

While Fe IRIS tubes were a great advancement in wetland science, many environmental researchers were interested in developing the same type of paint for manganese (Mn). Because Mn is a more energetically-favorable electron acceptor for reducing bacteria, Mn tubes could theoretically signal an earlier onset of suboxic
conditions than Fe tubes. An Mn IRIS tube was especially sought after for use identifying areas of denitrification\textsuperscript{90}. Birnessite was identified as a Mn oxide that could be used for Mn IRIS tubes because it is very abundant in soils and had been synthesized in previous works\textsuperscript{91–94}, but much like the development of the Fe oxide paint, the initial paints did not show sufficient adhesion to PVC tubes. Many of these methods also required the use of strong acids and extreme temperatures, which was not ideal. In 2013 an easy safer method of birnessite synthesis was introduced by Händel \textit{et al.}\textsuperscript{95}. This method was used by Dorau and Mansfeldt in 2015 to create a Mn IRIS device, however the process of painting was extremely time consuming compared to the previous work on Fe IRIS devices and adhesion to tubes was not sufficient. Rabenhorst advanced this technique when he discovered that the method of Händel \textit{et al.}\textsuperscript{95}, in which a 0.89 molar ratio of sodium lactate/KMnO\textsubscript{4} was used resulted in mainly poorly-crystalline birnessite; if a much higher molar ratio was used (11.1) followed by centrifugation, washing and dialysis, the suspension would contain a more crystalline birnessite\textsuperscript{90}. This more crystalline birnessite was easier to paint onto the tubes and had better adhesion to PCV tubes\textsuperscript{90,96}. While Mn IRIS devices were a great step forward and have proved very useful, quantifying Mn paint removal has proven challenging in soil environments.

\textit{Quantification of Paint Removal}

Quantification of paint removal on tubes was another factor in the development of IRIS that has changed considerably since their invention. Initially, visual assessment was used to determine paint removal by comparing films with standard charts. This visual
method works as a quick assessment in the field but was shown to be quite subjective\textsuperscript{97}. A more accurate assessment was needed, especially when conducting research\textsuperscript{89}.

Several approaches have been developed for assessing paint removal. A tracing method was used in which a clear thin plastic was wrapped around the tube and the areas of reduction were traced, and the traced area was scanned and analyzed using free image analysis software\textsuperscript{93}. This method worked but was extremely time consuming. Digital scanning of the tube with a computer scanner was possible, but very problematic due to the cylindrical nature of the tube. Handmade equipment was necessary to scan tubes, and multiple scans were needed to get a picture of the entire tube; individual scans then needed to be pieced together using Photoshop or similar software and analyzed using image analysis software like ImageJ or Image Tool 3.0\textsuperscript{89,98–100}. This type of digital analysis was not easy, required a lot of equipment and could not be done in the field. A visual grid method was also developed that could be used in the field and was more consistent from person to person than the visual assessment without a grid. For the visual grid method, a grid pattern is printed on a mylar transparency. The grid is then wrapped around the IRIS tube and the operator marks squares that have at least 50\% removal. The grid can then be removed and counted in order to obtain a removal percentage for a 360-degree section of the IRIS tube that is much more accurate than previous visual methods\textsuperscript{101}. The grid method was shown to agree very strongly with paint removal rates using the image analysis method\textsuperscript{101}. Still, the grid method required marking and counting squares, which was time consuming and subjective. Image analysis was preferable, but
difficult due to the cylindrical nature of IRIS tubes which made the grid method a viable method for paint removal quantification over visual assessment[^101].

**Development of IRIS Films**

While Fe and Mn IRIS tubes are extremely useful, as previously described, analysis can be difficult. Even when using the improved methods of paint synthesis, paint on tubes could be abraded during transport and insertion, especially in sandy soils[^100]. Additionally, an issue arose with sustainability. Because paint on IRIS tubes could not easily be removed and repainted and each tube is a section of 1-inch PVC, there is unnecessary environmental impacts with the use of tubes. Some researchers tried to use IRIS paint on flat surfaces like plastic sheets, but there was not an installation method for the flat and flimsy material that did not involve disrupting the soil profile[^100]. This led Rabenhorst to develop a system for making and deploying oxide-coated plastic films referred to as IRIS films[^100]. In his initial study, Rabenhorst tested four different types of plastic films and concluded that a white 10 mil PVC film that was flexible enough to manipulate, but rigid enough to promote soil contact after insertion was the optimal choice[^100].

Films have several advantages over tubes. Not only are they less expensive and result in less waste, but painting of the films is easier and faster than tube devices. Because the PVC sheets are available in different sizes, multiple films can be cut from one sheet. PVC sheets can be painted by hand using a foam brush and taking care to apply an even coating to the entire sheet. Masking tape can be used along the top edge to ensure a clean line at the top of each film. A hole punch is used to cut 6-mm holes about
2 cm from the bottom of each film. These holes are used in the deployment process. This method of making IRIS films is easier as it requires less equipment than the previous method for painting tubes.

Once made, IRIS films are much easier to store, transport, and install than the previous IRIS tubes. Because the films lie flat, many can be prepared and stored in a relatively small area. Inserting the film requires some equipment that is reusable and easy to use. First, the painted film is inserted in to a clear 1-inch polycarbonate tube. A pilot hole is made in the soil where the film is to be placed. Depth of the hole is dependent on the length of the film. A push rod equipped with a hook is inserted into the tube and the hook is placed inside the hole that was punched out of the film. This push rod allows the operator to insert the tube and the push rod into the pilot hole and hold the film in place while the tube is removed. The film will then unroll and fill the pilot hole and make contact with the soil surface inside of the hole.

Quantification of paint removal was also shown to be more straightforward using films compared to tubes. Films can be easily scanned with an unmodified flatbed scanner, which greatly improved analysis using image analysis tools previously used on tubes and described above. Visual assessment of films could still be done in the field but image analysis has been shown to be much more accurate. Digital analysis of IRIS films has been adopted over the grid or visual methods due to its accuracy and ease of use, however, digital analysis requires a lot of equipment and there is a level of technical knowledge necessary to analyze individual images which could not be easily disseminated to farmers. For these reasons my research aimed to test different
quantification methods including the grid method and a modified digital method that might be more feasible for widespread use of IRIS films by farmers, especially in developing countries.

Conclusion

As previously mentioned, the IRIS technology has been an integral advancement in wetland science and the classification of anaerobic soil environments. Many researchers have used IRIS in unique ways\textsuperscript{90,102–104}, but none have used them to monitor AWD management in rice. My research aimed to explore the use of IRIS films as a tool to aid in AWD management and decrease As mobility in rice paddy soil. Additionally, I will explore factors related to implementing such a technology in the developing world where As in rice is a major concern and access to resources is limited.
Chapter 2

FIELD STUDY AND QUANTIFICATION METHODS

Introduction

Arsenic (As) and cadmium (Cd) are toxic and nonessential for life\textsuperscript{1,58}, thus, their accumulation in rice grain poses a serious threat to food security and human health\textsuperscript{7,58}. Rice is a staple crop for billions of people around the globe, especially in developing countries and in Asia where 90 percent of the world’s rice is produced and consumed\textsuperscript{105}. Paddy rice is prone to As uptake because it is grown in flooded soil, which leads to reducing conditions that increase As mobility through reductive dissolution of As-bearing Fe and Mn oxides\textsuperscript{38}. While growing rice with less soil flooding limits As release, this practice may decrease yield and increase Cd release. Thus, strategies to limit both As and Cd are necessary.

Alternate wetting and drying (AWD) is a water management method that can limit As and Cd concentrations in rice grain while saving water and reducing greenhouse gas emissions\textsuperscript{57,62,64}. However, the ability of AWD to decrease As and Cd concentrations in rice grain is inconsistent across soils and can be difficult to manage. AWD utilizes periodic drying cycles during flooded rice production. Adding drying cycles creates oxidizing conditions that promote the precipitation of Fe and Mn oxides and subsequent retention of As, which limits As mobility and availability for plant uptake\textsuperscript{63,84}. Because
Cd is more available in oxic conditions and severe drying has been shown to reduce grain yield, AWD must be carefully managed in a site-specific manner to prevent undesirable consequences\textsuperscript{71,81}. Redox potential (Eh) measurements can indicate the extent of reducing conditions that promote reductive dissolution of Fe and Mn oxy(hydr)oxide minerals\textsuperscript{82–84}, but the electrodes are expensive and not feasible for rice farmers to use. Therefore, a low-cost, practical tool to measure reducing conditions in rice paddies is critically needed.

Indicator of redox in soils (IRIS) films were developed and used to delineate hydric soil conditions, and these devices could be a low-cost option for rice farmers to better manage AWD. IRIS films consist of a thin, white vinyl sheet that is coated with Fe or Mn oxide mineral paint that has been synthesized in a suspension. These “IRIS paint”-coated sheets can be cut to the desired film size and easily inserted into soil\textsuperscript{100}. If soil conditions are reducing, the Fe or Mn oxides will be reductively dissolved and removed from the film over time. Once removed, IRIS paint removal can be quantified to indicate the severity of reducing conditions in soil\textsuperscript{87,100}. However, it is currently unknown how paint removal compares to Eh conditions of paddy soils under AWD management, for how long the films would need to be inserted to show a response, and how robust the quantification methods are.

Here, we explored the use of Fe and Mn IRIS films to indicate reducing conditions in paddy soil under AWD management. To our knowledge, the IRIS technology has never been used in rice systems so there are a lot of unknowns in terms of IRIS film response to film residence time and different AWD treatments. Therefore, our objective was to evaluate the effectiveness of IRIS films in paddy soils in comparison to
other indicators of redox potential under different AWD treatments. Additionally, quantification of paint loss from IRIS devices is presently done using a grid system\textsuperscript{101} or by scanning or photographing the films and analyzing the image using ImageJ software\textsuperscript{100}. Both of these methods of quantification are reliable, but also time consuming and subjective. The image analysis method is favored to the grid method; however, it requires many steps to analyze one film including converting the film image to greyscale in Photoshop, then using ImageJ to select a threshold that separates the image into two categories of what the operator thinks is substantially removed and what is not\textsuperscript{100}. The binary images that are created in ImageJ can then be analyzed and measured in ImageJ to give a value for percent paint removal\textsuperscript{100}. While this method works and is an improvement over the visual assessment method and the grid method, it still requires the operator to select what they think is the correct threshold to represent removal, which can introduce human error and requires a lot of knowledge that cannot easily be transferred from person to person. Here, we developed a new system of quantification entitled IRIS Imager, which utilizes an in-house code on MATLAB software. IRIS Imager, when given an image of a starting film with no removal and an image of an ending film with removal, analyzes them by finding the change in lightness of each individual pixel from the starting image to the ending image using LAB color space. This method only requires the operator to input the desired images and select the corners of the films in order for IRIS Imager to match the starting image to the ending image. This way the operator never has to decide what paint was removed and what was not, making it less subjective than other methods. We hypothesized that IRIS Imager is more objective and delivers quality data
quickly and efficiently compared to current methods of quantification. As such, IRIS Imager could be applied more broadly allowing IRIS films to be used as a low-cost approach to better manage AWD in As-prone areas.

**Materials and Methods**

*Field Setting*

These studies were conducted in existing rice paddy mesocosms at the University of Delaware RICE facility as described by Limmer *et al.* Briefly, the facility includes 30 - 2x2 m rice paddy mesocosms that are lined with pond liners and backfilled with the native Ultisol soil. These soils are highly weathered, contain a high percentage of Fe oxides, and are common in much of the Southeast and Mid-Atlantic United States; soils are also representative of those found in Southeast Asia where a large amount of rice is grown. An irrigation system using municipal water and submersible pumps with float switches were used to control water management in each paddy. Paddies were also equipped with water measurement monitoring wells made of perforated PVC piping like those typically used in AWD. Continuous redox probes which were installed at depths of ≈5 and ≈10 cm relative to the soil surface were monitored using a data logger (Figure 2.1). Our work takes advantage of an ongoing field investigation of silicon rich plant-based amendments, which include, fresh rice straw or husk, charred rice straw or husk, or a mixture of the two scenarios and allowed us to target different paddies of the same soil type with differing redox states.
Figure 2.1: Depiction of rice paddy mesocosms at the University of Delaware RICE facility. Paddies are lined with pond liners and backfilled with native Ultisol soils. Paddies are equipped with an irrigation system, pump and float switch to manage water levels, water measurement wells, continuous redox probes, and porewater samplers.

Preparation of IRIS Paint and Films

Iron and Mn IRIS paints were synthesized using the methods described previously\cite{96,106}. Films consisted of rigid white vinyl sheets (p/n RVW1018, Coast to Coast Label, Fountain Valley, CA, USA) that were evenly painted and cut to be 7.5 cm wide and 30.5 cm long. A 5-cm non-painted rectangle remained at the top of each film for ease of retrieval.

Field Study 1: Film Residence Time

Because IRIS films had never been used in the rice paddy environment, an experiment was conducted to assess the residence time necessary to observe removal on both Fe and Mn films. We tested two removal frequencies for both Fe and Mn films using 8 Fe films and 8 Mn films per paddy: 6-hour extraction intervals in paddies.
amended with rice straw and 12-hour extraction intervals in paddies amended with charred straw. We chose these frequencies and corresponding Si amendments because we expected Si amended fresh straw paddies to become reducing faster than charred straw paddies. This study allowed us to understand the timing needed for IRIS films to indicate reducing conditions in rice paddies under AWD. Films were installed into the paddies during a dry cycle and paddies were immediately reflooded.

Field Study 2: AWD

Two severities AWD were tested following harvest of the 2019 rice growing season to mimic “severe” and “safe” AWD\textsuperscript{63} in order to evaluate the use of IRIS films across a spectrum of redox conditions. For severe AWD, the water level in the paddies was monitored using the water measurement wells, and soil was allowed to dry to 30 cm below the soil surface. For safe AWD, the paddies were allowed to dry to 15 cm below the soil surface\textsuperscript{63}. For both severe and safe AWD, 8 Fe and 8 Mn coated IRIS films were installed in 6 different paddies, three with fresh straw Si amendments and three with charred straw silicon amendments; a total of 48 Fe films and 48 Mn films were installed under both safe and severe AWD. Films were installed into dry paddies and once films were installed in to all 6 paddies, they were immediately reflooded to \textasciitilde 5 cm above the soil surface. Films were installed and removed in a grid pattern with alternating Fe and Mn films in 4 rows (2 Fe and 2 Mn films per row) (Figure 2.2). Iron films were removed from paddies every 12 hours while Mn films were removed from paddies every 6 hours, based on results from Field Study 1 (film residence time experiment).
Figure 2.2: IRIS films were inserted into each rice paddy in a grid pattern, four rows of films, 2 Fe and 2 Mn per row. In the graphic on the left, green hexagons represent rice plants or root structures left after harvest. Brown circles represent Mn films and yellow circles indicate Fe films and the orange circle in the top left corner represents the irrigation pump. Films were removed in the same order they were placed, left to right starting in the bottom left so that the last film removed was from the top right.

Porewater Collection

Porewater samples were obtained at film insertion (t = 0) and every 12 hours thereafter for 96 hours using ceramic porewater samplers (p/n 1910PL06 from Soilmoisture Equipment Corp., Goleta, California). Porewater samplers were inserted into the soil at approximately a 45° angle to a depth of ≈13 cm and left in place for the duration of the study. Porewater was collected using vacuum locking syringes; three sample line volumes were purged prior to sample collection. Porewater redox was immediately measured following collection using a calibrated probe (Orion 9179BNMD)
and pH was measured using a calibrated electrode (Orion 8107BNUMD). A portion of each porewater sample was immediately transferred to sample vials for Fe(II) and Mn(II) colorimetric quantification using the ferrozine and periodate methods, respectively\textsuperscript{107,108}.

**Quantification Methods**

Paint removal on IRIS films from the AWD study was quantified using two different methods. First, a slightly modified version of the grid method previously used for IRIS tubes was used\textsuperscript{101}. Films were placed under a grid printed on transparent mylar film with 864 grid squares (54 squares x 16 squares) where each individual square measured $\approx 0.5\text{-cm}^2$. Grid squares with what looked to be at least 50% paint removal were considered removed. Percent paint removal was quantified for the entire film, and in order to evaluate spatial variability within films, percent paint removal was also quantified for the top 13 cm and bottom 13 cm of each individual film.

Second, films were scanned using a flatbed scanner and analyzed using MATLAB software with an in-house code that we call IRIS Imager. For this, initial films were scanned using a digital scanner pre-insertion and again post-removal. IRIS Imager then compared the initial and post-removal film scans to estimate paint removal based on the change in lightness of each individual pixel. Additionally, we developed IRIS Imager to identify Fe on Mn films using the hue change from the starting image to the ending image in order to mitigate some of the uncertainty and subjectivity of Mn film removal quantification due to Fe oxide precipitation onto Mn films (as described in the results). IRIS Imager can examine the images of the ending films, identify any Fe pixels and count them as 100% Mn removal.
Validation of the IRIS Imager method

In order to validate the novel IRIS Imager method, we used IRIS films from a previous 2018 study (data not shown), which was our first experience with the IRIS technology. We were able to use the information we gathered from that study as the basis for the AWD study shown here and to better understand the quantification methods and improve upon IRIS Imager. Both IRIS Imager and the grid method were used to determine percent paint removal from the films. These results were compared to quantities of remaining Fe or Mn obtained through destructive extractions of Fe and Mn films. Extractions for Fe films were done using a dithionite citrate bicarbonate (DCB) solution, modified from Taylor and Crowder109. The Mn films were extracted using 0.5 M hydroxylamine HCl which has been shown to reductively dissolve Mn paint from films while leaving any precipitated Fe100. The resulting Fe or Mn extraction solutions were then analyzed using ICP-OES. Percent removal for films was calculated by comparing Fe and Mn concentrations from ICP analysis to Fe and Mn concentrations on initial films. This initial concentration was attained by extracting 6 initial Fe and 6 initial Mn films that were prepared in the same way as films used in the study but were never deployed in the field. An average of the 6 films was used for the initial film concentration. Extraction concentrations of Fe and Mn films were then compared to the theoretical initial Fe and Mn film concentrations, respectively. To our knowledge this type of extraction and ICP analysis has never been applied to IRIS films and should provide a valuable comparison to validate other quantification methods.
In order to further validate the novel IRIS Imager method, films were painted with decreasing amounts of Fe or Mn paint to create a standard curve to represent removal from 10% to 90% (Figure 2.2). This test was conducted in triplicate and films were analyzed in IRIS Imager using the film with the most paint initial film (0% removal) as the starting image and the standard film (10-90% removal) as the “post-removal” image. IRIS Imager output removal was compared to removal calculated by film extraction and ICP–OES analysis using linear regression.

**Statistical Analyses**

Correlations between film paint removal and porewater chemistry were determined using Pearson correlation coefficients. All data were analyzed using JMP Pro 14.

**Results**

*Field Study 1: Film Residence Time*

To test film residence time, we utilized two paddy management strategies that varied in redox state—rice straw and charred straw amendments. In fresh straw paddies, for which we expected to become reducing faster than charred straw paddies, 6-hour extraction intervals for Fe films did not result in measurable paint removal until the 48-hour interval (20% removal) (Figure 2.3). In contrast for charred straw paddies, for which we expected to become reducing slower, only 5% removal occurred on Fe films by 48-hours and it took 96 hours for films in these paddies to show 20% paint removal. Because
we expected charred straw paddies to reduce slower than fresh straw paddies, there is little benefit to removing Fe films sooner than 12 hours in less reducing soils. For Mn films, 6-hour extraction intervals in fresh straw paddies allowed us to observe a progression of removal over time from 1% at 6 hours to 35% at 24 hours and up to 80% in just 48 hours. The use of 12-hour extraction intervals exhibited large amounts of removal in 24 hours (45%) even in what we expected to be a slower reducing charred straw paddy (Figure 2.3). This led us to use 12-hour extraction intervals for all Fe films and 6-hour intervals for all Mn films in subsequent studies in order to observe a gradual progression of IRIS paint removal over time for both Fe and Mn films regardless of paddy Si treatment.

Figure 2.3: Progression of Fe (left) and Mn (right) paint removal from IRIS films installed in rice paddies amended with fresh straw (top) or charred straw (bottom). Removal and evaluation of Fe and Mn films at 12 and 6-hour intervals, respectively, is adequate to observe detailed progression of paint removal.
Comparison of Quantification Methods

In the AWD field study, % removal for Mn was lower than for Fe, which allowed better comparison of the IRIS Imager and grid methods over a wider range of values than each type of film (Figure 2.4A). The IRIS Imager and grid methods were strongly correlated when all data was considered ($r^2 = 0.94$) and when Fe films ($r^2 = 0.95$) and Mn films ($r^2$ of 0.935) were considered separately and all matched closely with the 1:1 line (Figure 2.4).
Figure 2.4: Relationship between the IRIS Imager and grid methods of paint removal quantification for the AWD study for (A) All Fe and Mn combined, (B) Fe films, and (C) Mn films. Blue dashed line is the linear trendline and the black solid line is a 1:1 reference line.
Total extraction analysis found that initial paint concentrations on films was reproducible with \( \approx 2\% \) relative standard deviation for both Fe and Mn films which showed that when prepared carefully, films have an even coating of paint. Our analysis of the different quantification methods showed a stronger correlation between Fe films \((r^2 = 0.76)\) compared to Mn films \((r^2 = 0.351)\) for both the IRIS Imager method and grid method. Additionally, the grid method had a slightly stronger relationship to the film extraction method than the IRIS Imager method for both Fe and Mn films (Fe Films: grid \( r^2 = 0.86 \) IRIS Imager \( r^2 = 0.76 \), Mn films: grid \( r^2 = 0.55 \), IRIS Imager \( r^2 = 0.35 \)) (Figure 2.5). Most data points were positioned above the 1:1 line with the exception of the comparison between IRIS Imager and the grid method which crosses over the 1:1 line (Figure 2.5A) and the grid method to the extraction method, which was situated below the 1:1 line (Figure 2.5F). The grid method and IRIS Imager methods had strong correlations with each other in both Fe and Mn films (Figure 2.5), which agrees with grid and IRIS Imager comparisons from the AWD study described above (Figure 2.4).
Figure 2.5: Relationship between three different quantification methods for both Fe (orange circles) and Mn (brown squares). (A, D) IRIS Imager vs. grid, (B, E) IRIS Imager vs. Extraction, (C, F) grid vs. Extraction. Extraction % removal, described previously, was quantified by calculating the concentration difference between post removal films and a calculated initial film concentration. All units are percent IRIS paint removed from films. Blue dashed line is the linear trendline and the black solid line is a 1:1 reference line.
The IRIS Imager quantification outputs showed strong relationships with standard films that had been extracted using the methods described above. Paint quantification was slightly better for Fe ($r^2 = 0.94$) than Mn ($r^2 = 0.89$, Figure 2.6). While the relationship for Fe followed closely to the 1:1 line and crossed above only for higher removal rates, the relationship for Mn was below the 1:1 line suggesting that partial Fe removal that is very light in color is harder for IRIS Imager to quantify while Mn quantification may be more difficult for mid-range removal rates (Figure 2.6).

![Figure 2.6](image)

**Figure 2.6:** IRIS Imager method removal quantification compared to prepared standard film extraction removal rates for (A) Fe films, (B) Mn films demonstrates IRIS Imager’s ability to quantify IRIS paint removal based on color change. All units are percent IRIS paint removal from films. Blue dashed lines are the linear trendlines and the black solid lines are 1:1 reference lines.
Field Study 2: Data Analysis Based on Redox State

Paddies were numbered R1-R6 based on their average degree of oxidation or reduction for both the severe (>30 cm dry-down) and safe (15 cm dry down) AWD treatments combined. Paddies were labeled using porewater redox data with R1 indicating the overall most reduced paddy conditions and R6 signifying the overall least reducing (or most oxidized) paddy conditions.

Porewater Chemistry and Redox Measurements

Porewater redox potential (ORP) was higher under severe AWD than safe AWD (Figure 2.7). Continuous redox measurements also showed that ORP was initially higher in severe AWD and remained higher for most paddies compared to safe AWD (Figure 2.7B,D). Continuous redox measurements are shown at the depth of ≈ 5 cm while porewater redox was taken at ≈ 13 cm. We did observe some difference in redox data from porewater to the continuous probe as continuous measurements were generally lower than porewater redox measurements. Additionally, continuous probe data was unreliable for R2 in both severe and safe AWD and is not shown. However, the data still suggests that the paddies were allowed to become more oxidized under severe AWD than safe AWD. From the continuous redox data we can observe that under severe AWD, most paddies did not drop below 0 mV until ≈ 36 hours after reflooding, while under safe AWD most paddies dropped below 0 mV within 6-18 hours; with the exception of paddy R6 which we have observed as being the most oxidized of the 6 paddies (Figure 2.7B,D). Porewater pH under severe AWD was lower for all paddies at insertion than it was under...
safe AWD (Figure 2.8). Porewater pH under safe AWD hovered around neutral for all paddies (Figure 2.8B).

Figure 2.7: Redox potential (ORP) measurements were taken from porewater samples collected at film insertion (t = 0) and every 12 hours thereafter for the duration of the study. Continuous redox measurements were also taken using Pt electrodes and a data logger. Porewater redox was taken at ~ 13 cm and continuous probe redox is at a 10 cm depth. (A) Severe AWD porewater ORP. (B) Severe AWD continuous ORP. (C) Safe AWD porewater ORP. (D) Safe AWD continuous ORP. Grey vertical boxes in panel B and D represent the dry phase of AWD. Paddies were reflooded at t = 0.
Porewater Fe(II) and Mn(II) were generally higher for safe AWD compared to severe AWD with the exception of highly oxidized paddies R4, R5, and R6 (Figure 2.9). Porewater Fe(II) for severe AWD in all paddies except R1 ranged from 0 - 1.6 mg/L but hovered mostly around 0.5 mg/L for the duration of severe AWD; porewater Fe(II) concentrations in R1 never exceeded 5 mg/L. The safe AWD treatment showed similar results as severe AWD for more oxidized paddies (R4, R5, and R6), but had increases in porewater Fe(II) concentrations for more reduced paddies, especially R1, which ranged from 2 to nearly 42 mg/L (Figure 2.9A,C). Porewater Mn(II) followed a similar trend as Fe(II) for both severe and safe AWD however some Mn(II) was observed in all paddies like R4, R5 and R6 where Fe(II) remained low for both severe and safe AWD (Figure 2.9B,D). Generally, Mn(II) concentrations were higher than respective Fe(II)

Figure 2.8: Porewater pH measurements at film insertion and every 12 hours thereafter for 96 hours. (A) Severe AWD pH measurements. (B) Safe AWD pH measurements.
concentrations at specific IRIS film extraction intervals with the exception of R1 in the safe AWD treatment.

Figure 2.9: Porewater Fe(II) and Mn(II) was measured every 12 hours for the duration of each AWD regimen (severe and safe), 96 hours for Fe and 48 hours for Mn. (A) Severe AWD pore water Fe(II). (B) Severe AWD porewater Mn(II). (C) Safe AWD porewater Fe(II). (D) Safe AWD porewater Mn(II). Paddies are labeled in the order of least oxidized to most oxidized across both severe and safe AWD, R1 being least oxidized (more reducing) and R6 being most oxidized (least reducing).
IRIS Film Paint Removal

As expected, Mn films showed substantial paint removal due to soil reducing conditions earlier than Fe films. In safe and severe AWD treatments where both Fe and Mn films showed removal. The Mn films exhibited substantial removal within 24 to 36 hours after IRIS film insertion, while Fe films did not show substantial paint removal until at least 72 hours after film insertion (Figures 2.10-2.16). Paddies with higher initial redox potential did not exhibit much removal throughout the course of both severities of AWD with the exception of the 84 and 42-hour extraction intervals for Fe and Mn films respectively (Figures 2.15-2.16). Very little IRIS paint removal was observed on Fe films for the first 60 - 72 hours for both severities of AWD (Figure 2.10A,C). Similarly, very little paint removal was observed in the first 24 hours on Mn films in severe AWD. More Mn paint removal was observed during safe AWD in the first 24 hours with the exception of highly oxidized paddies R5 and R6 (Figure 2.10). Very little Fe and Mn paint removal was observed in paddies R5 and R6 for both severities of AWD, which was supported by the higher redox potentials and lower porewater Fe(II) and Mn(II) for those paddies (Figure 2.9, 2.10).
Figure 2.10: Percent paint removal reported from IRIS Imager for each individual IRIS film and paddy by extraction interval. (A) Fe paint removal for severe AWD. (B) Mn paint removal for severe AWD. (C) Fe paint removal for safe AWD. (D) Mn paint removal for safe AWD. Removal rates shown are those reported from IRIS Imager.
Figure 2.11: Visual representation of IRIS paint removal from R1. AWD treatment is listed on each picture as is extraction intervals and IRIS Imager percent paint removal.

<table>
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<td>2.5%</td>
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<td>36h</td>
<td>3.5%</td>
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</tr>
<tr>
<td>96h</td>
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Figure 2.12: Visual representation of IRIS paint removal from R2. AWD treatment is listed on each picture as is extraction intervals and IRIS Imager percent paint removal.

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<table>
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<th>R2 - Safe AWD - Mn</th>
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<tbody>
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<td>24.6%</td>
</tr>
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<td>48h</td>
<td>29%</td>
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</table>
Figure 2.13: Visual representation of IRIS paint removal for R3. AWD treatment is listed on each picture as is extraction intervals and IRIS Imager percent paint removal.

Figure 2.14: Visual representation of IRIS paint removal for R4. AWD treatment is listed on each picture as is extraction intervals and IRIS Imager percent paint removal.
Figure 2.15: Visual representation of IRIS paint removal for R5. AWD treatment is listed on each picture as is extraction intervals and IRIS Imager percent paint removal.

Figure 2.16: Visual representation of IRIS paint removal for R6. AWD treatment is listed on each picture as is extraction intervals and IRIS Imager percent paint removal.
Linear regression of average Mn IRIS paint removal over all extraction intervals to average Mn(II) in porewater, average porewater redox (all averaged by paddy) show a positive relationship between Mn paint removal and porewater Mn(II) \( (r^2 = 0.35, \ P = 0.04) \), and a negative relationship between Mn paint removal and porewater redox \( (r^2 = 0.33, \ P = 0.05) \) (Figure 2.17).

**Figure 2.17:** Linear regressions of Mn IRIS Imager paint removal averaged for all film extraction intervals vs. average porewater Mn(II), and average porewater redox. Mn paint removal is correlated to Mn (II) in porewater \( (r^2 = 0.35, \ P = 0.04) \) (A). Mn paint removal is negatively correlated to porewater redox \( (r^2 = 0.33, \ P = 0.05) \) (B). Blue dotted line represents the linear trendline of both safe and severe AWD points together.

**Spatial Variability of IRIS Paint Removal**

Spatial variation in IRIS paint removal was observed between paddies, extraction intervals, and on individual films; however, some trends were apparent. On average, more IRIS paint removal was observed on the bottom half of Mn films in safe AWD
compared to the top of films in safe AWD, and the tops and bottoms of Mn films in severe AWD. (Figure 2.18). For Fe films, there was no apparent trend for the top of films versus the bottom of films. Additionally, an orange color can be observed on portions of Mn films, especially on the bottom half of films in the safe AWD treatments (Figure 2.11-2.14). A uXRF image of an Mn film with this orange color surrounding a spot of Mn IRIS paint that had not yet been reduced provided evidence that the orange color on the Mn films was due to the reprecipitation of Fe (Figure 2.19)

Figure 2.18:  Average IRIS paint removal from the top half and bottom half of films showing the distribution of paint loss on films. (A) Average Fe paint removal by extraction interval for both dry downs. (B) Average Mn paint removal by extraction interval for both dry downs. Error bars represent max and min.
Figure 2.19: uXRF image taken of a Mn film with Fe precipitated around a patch of Mn IRIS paint that had not yet been reduced. This agrees with previous findings that the orange color sometimes seen on Mn films is precipitated Fe.

Discussion

The objective of this study was to evaluate the possible use of IRIS films in rice paddies to aid in AWD management. IRIS films have advanced the classification of hydric soils\textsuperscript{87,88}, but to our knowledge, they had not been used to indicate reducing conditions in rice paddies under AWD. Thus, we conducted a series of tests to better understand timing of paint removal and spatial variability within rice paddies and on individual films over time and in different water management strategies. Because having a reliable way to quantify IRIS paint on films is important, we also tested a new quantification method: IRIS Imager.
Our study tested two AWD regimens: safe AWD where rice paddies are drained to \( \approx 15 \) cm below the soils surface, and severe AWD where we allowed the same rice paddies to drain \( > 30 \) cm below the soil surface. We hypothesized that IRIS films would be a better indication of soil redox potential over different AWD management strategies than water measurement wells currently used in AWD management. Our goal was to establish indicator of redox in soils (IRIS) films as a tool that farmers could use in place of expensive electrodes to measure and identify reducing conditions in paddy soils. To that end, our objective was to evaluate paint loss on IRIS films in relation to other indicators of reducing conditions and to better understand how long it takes for rice paddies to become reducing once they are reflooded after different severities of AWD.

**Validating the Novel IRIS Imager**

Strong relationships that are close to 1:1 lines between IRIS Imager outputs and standards films as well as strong relationships between IRIS Imager outputs and the grid and extraction methods indicate that IRIS Imager can accurately quantify both Fe and Mn IRIS paint loss on films. Stronger correlations for Fe films compared to Mn films from all validation methods (grid, extraction, and standard tests) suggest that IRIS Imager may do a slightly better job at quantifying paint loss on Fe films opposed to Mn films; however, this trend was observed for grid method as well. Mn films appear more challenging to accurately quantify using the grid method at least in part because of Fe precipitation on areas of Mn removal (e.g., Figure 2.12, 2.19). Some discrepancies between IRIS Imager quantification outputs and the extraction method quantification outputs could be due to partial removal of Fe and Mn paint as the standard tests showed IRIS Imager was less
accurate with higher removal rates for Fe films and in the mid-range removal rates for Mn films (Figure 2.6).

Fe Precipitation on Mn Films

Previous visual assessment of Mn IRIS films and μXRF images performed here have demonstrated that orange spots on Mn films after film removal from reducing soils is precipitated Fe\textsuperscript{100} (Figure 2.19). We believe the Fe precipitation on Mn films occurs because Mn oxides are strong oxidants that have the ability to oxidize Fe(II) in porewater\textsuperscript{110}. As Mn oxides on the film oxidize Fe(II) allowing it to precipitate on the film, Mn oxides are reduced to Mn(II) and migrate into soil solution. Precipitated Fe on Mn films makes paint removal quantification using the grid method much more difficult to interpret. It is sometimes hard to distinguish the point where Mn paint ends and precipitated Fe begins, but it has been shown that areas of Fe precipitation also represent areas of total Mn removal\textsuperscript{111}. Because IRIS Imager was developed to identify Fe precipitation on Mn films using hue change from starting to ending images as described previously, IRIS Imager may be better able to account for Fe precipitation on Mn films because the program is less subjective and automatically counts Fe precipitation as 100% Mn removal without the possibility of human error.

Even still, our studies suggest that paint loss on Mn films is harder to quantify than on Fe films due to Fe precipitation on Mn films, and there tends to be more spatial variability in Mn paint removal than Fe paint removal. Because it is harder to quantify Mn paint removal, and because reductive dissolution of Fe oxides are thought to be the
main driver of As release into pore water\textsuperscript{48,49}, Fe films may be a better tool for farmers to use in AWD management than Mn films.

\textit{Variation Between Quantification Methods}

Some variation in paint removal rates from method to method can be explained. For instance, a small amount of variation between IRIS Imager and the grid method is most likely due to abrasion on films during insertion and removal. This abrasion appears as long vertical scratches unusually down the center of films and can be observed on most films in Figures 2.10-2.15. While the grid method can allow the operator to ignore abrasion, IRIS Imager removal is quantified based on each individual pixel from the starting image to the ending image and with a pixel size of roughly 0.127 mm\textsuperscript{2}, abrasion is usually counted as 100\% removal. This can result in typically a 2-3\% increase in IRIS Imager removal outputs compared to the grid method. This slight overestimation of removal with IRIS Imager was observed in the first few intervals for each paddy, specifically R1 (Figure 2.13), where nearly no removal occurred but IRIS Imager reported slight removal due to abrasion.

Additionally, partial paint removal can be difficult to quantify with both IRIS Imager and the grid method. On some Fe films, light yellow patches were observed that are likely goethite left after the preferential removal of ferrihydrite from the film\textsuperscript{112}, and it is subjective to decide if that observation should count as removal with the grid method. IRIS Imager removes subjectivity while delivering results that are more accurate based on the standard film tests we performed (Figure 2.6) and method comparisons reported here (Figure 2.4). Standards tests (Figure 2.6) and strong relationships between IRIS
Imager and grid data for our field study (Figure 2.4) suggest that IRIS Imager is a robust alternative of IRIS film quantification.

**IRIS Film Paint Removal Across a Range of Paddy Conditions**

Our film residence time experiment and our study with two AWD treatments provided a range of redox conditions under which Mn and Fe paint removal on IRIS films could be observed in rice paddies. The film residence time experiment led us to choose 12-hour extraction intervals for Fe films and 6-hour intervals for Mn film extraction. As we expected, Mn films showed greater paint removal at a much faster rate than Fe films. The Fe films only showed $\approx 20\%$ removal by the end of both extraction intervals and Si treatments while Mn films exhibited over 80% removal by the last extraction interval for both Si treatments and in a shorter period of time for charred straw Si treatments (Figure 2.3). The residence time experiment helped us to conclude that IRIS films in rice paddies under the same water management but different soil conditions may have very different removal rates.

Our AWD field study results were very promising for the possible use of IRIS films in rice paddies. Linear relationships between average Mn removal over all extraction intervals and average porewater Mn (II) (Figure 2.17A) and redox potential (Figure 2.17B) suggest that Mn paint removal is correlated to porewater Mn (II) and soil redox. The same correlations were not found for Fe films, possibly due to the lack of Fe paint removal on films in the duration of the study. It is possible that stronger correlations could be seen if the study was extended to include more removal intervals past those shown here in order to see more Fe paint removal over time.
Some relationship can be seen between paddies with low Fe and Mn paint removal rates and pore water Fe(II) and Mn(II), as well as higher redox potential. Paddies that were more oxidized at the start and throughout both AWD treatments (R5 and R6) exhibited very little paint removal with no more than 25% for Fe and Mn films (Figure 2.10, 2.15, 2.16). This lack of IRIS paint removal corresponded to low Fe(II) levels in pore water for R5 and R6 (0.40 – 1.2 mg/L for severe AWD and below the detection limit to 0.5 mg/L in safe AWD) and relatively low Mn(II) levels (2.6 – 8.0 mg/L in severe AWD and 2.7 – 15.6 mg/L in safe AWD) (Figure 2.9). Paddies R5 and R6 also exhibited relatively high redox potential with the lowest porewater redox values for safe AWD at 152 mV in R5 and 144 mV in R6 (Figure 2.7). For severe AWD, the lowest porewater redox potential for R5 and R6 were 166 mV for R5 and 138 mV for R6 (Figure 2.7).

Paddy R4 could also be considered a more oxidized paddy specifically in severe AWD as little to no paint removal was observed in the first 60 hours for Fe films and 30 hours for Mn films. Additionally, porewater Fe(II) remained very low in R4 during severe AWD only ranging from 0.4 - 0.8 mg/L and Mn(II) in R4 during severe AWD was also relatively low ranging from 2.5 - 6.2 mg/L. Starting porewater redox potential for R4 during severe AWD was the second highest at 399 mV, which likely affected the ability of reducing bacteria to become active in the soil.

Paddies that were not as oxidized initially and throughout the course of the studies (R1, R2 and R3) also exhibited higher Fe(II) and Mn(II) in porewater for safe AWD treatments in relation to the more oxidized paddies (Figure 2.9 A and C). Fe(II) and Mn(II) for severe AWD treatments were low for all paddies and ranged 0.62 mg/L – 4.71
mg/L for Fe (II) and 3.8 mg/L – 10.7 for Mn(II) (R1, Figure 2.7A,C). However, this
distinction between R1 and other less oxidized paddies (R2 and R3) did not present itself
in IRIS paint removal rates (Figure 2.10). This disconnect between IRIS paint removal
and porewater chemistry could be a result of the heterogeneity of soil as porewater
samples were taken from one stationary spot in paddies for the duration of the study.

For safe AWD, Mn films exhibited small amounts of removal earlier (6 hours)
than films under severe AWD (24 - 30 hours) and paint removal in safe AWD tended to
be concentrated on the bottom half of the films, especially in R1 – R4 (Figure 2.18). This
is most likely because the less extensive dry down allowed reducing conditions to remain
in the depths of the paddies below 15 cm. Because the IRIS films installed were only
about 30.5 cm long, upon reflooding reducing bacteria were already thriving in the lower
depths and able to reduce soil Fe oxides adjacent to the bottom of Mn films upon
insertion. The Mn oxides on the film could then oxidize the porewater Fe(II) as they
dissolved. This phenomenon is an example of how IRIS films are a robust way to obtain
a better understanding of redox in one location at different depths using one low-cost
device87. Measuring redox using other tools such as probes and porewater require
multiple measurements at many depths, which is not feasible for farmers.

While we observed an expected increase in paint removal over time for most of
the study, there was a decrease in removal for the last extraction interval for both Fe and
Mn films. This is partially attributed to the heterogeneity of soil, but also to the
placement of the films within the paddy. Films were inserted and removed in a grid
pattern and films from a specific extraction interval were removed from the same general
location in each paddy, whereas porewater samplers and continuous redox probes remained stationary and did not necessarily reflect the same microenvironment as each film. The second to last extraction interval was situated in the same corner of the rice paddies as our pump system which could have had an effect on oxidation of the soil as well as microbial communities in that area. As we drain the paddies using the pumps, water flows in channels along the outside of the paddy. Often, water pools near the pump and this area may not dry down as quickly as other areas in the paddy (pump location shown in Figure 2.2). This could allow reducing bacteria to survive in this area longer than the rest of the paddy, which would explain a sudden increase in removal rates at this location and a decrease in the next location away from the pump. This sudden increase in paint removal along with other increases or decreases in paint removal over time may not be reflected in porewater redox, Fe(II) and Mn(II) because throughout the studies porewater was taken from one location that did not change for the duration of the studies. Further research would have to be done to validate this explanation for the sudden increase and subsequent decrease in removal rates.

Our goals of the AWD field study were to determine if different AWD regimens were sufficient enough to slow Fe reduction and if IRIS films could signal reducing conditions in rice paddies. In current use of IRIS films, the devices can be installed at any time to evaluate reducing conditions in soil and they can be left there for weeks to a month at a time\textsuperscript{99,112}. As we have shown, the use of IRIS films in rice paddies under AWD would require farmers or researchers to insert their desired number of films into the paddies directly before reflooding and films would need to be removed days later.
rather than weeks. Our data suggests that in our particular soil type, significant Fe IRIS paint removal is present ≈72 – 96 hours after reflooding. Our results suggest that in practice, a Fe IRIS film may not need to be removed from a rice paddy until 72 hours after reflooding. Additionally, if little to no removal is observed, the next film could be removed after 24 hours rather than after 12 hours. Because the development of reducing conditions is extremely variable, farmers and researchers that might be interested in using IRIS films in rice paddies would have to gauge this timing in their own fields and their AWD management may not be the same from field to field. Researchers implementing safe AWD with only 15 cm dry downs may begin to see removal on films sooner than those using severe AWD.

The spatial variability observed in paint removal between and within paddies and on individual films may be considered an obstacle for implementation of IRIS films in paddy soil. This study utilized 6 different rice mesocosms under a range of soil management to capture varying soil characteristics that approach field conditions but are small compared to field conditions. Irrigated rice farms are generally small in comparison to other crops with most ranging between 0.5 and 2 hectares\textsuperscript{113}. Some farms are smaller like in Indonesia and Thailand, where a majority of farmers are cultivating only 0.1 to 0.5 hectares\textsuperscript{113}. However larger mechanized farms do exist in more developed countries like Argentina where the minimum farm size is \textasciitilde 50 hectares\textsuperscript{113}, and in the United States where the average rice farm is \textasciitilde 150 hectares\textsuperscript{114}. Even for farmers who only cultivate 0.1 to 0.5 hectares of land, multiple IRIS devices would need to be inserted in multiple parts of the field depending on how uniform the land is. In order to capture some of the spacial
variability in rice paddies farmers would need to install IRIS films in varying locations that are representative of field conditions. If the farmer knows there are low spots and high spots in the field, films would need to be placed in both of those areas. This would allow farmers to monitor reducing conditions as well as severe drying in high spots that may damage the rice crop. The number of replicate films per paddy would have to be a function of field size and known variability, specifically in the gradation of the field. Additionally, multiple films would need to be inserted into each replicate area.

While this approach with multiple films and replicates in one rice paddy may be a barrier of implementation for some farmers, it should provide a more robust indication of the reducing conditions that drive the release of As in to porewater because current AWD management only utilizes one water measurement well that is meant to be placed in a representative place in the field\textsuperscript{63}. Farmers currently practicing AWD are already making decisions for an entire field based on one measure of water depth in one area of that field. Additionally, for researchers interested in the spacial variability of reducing conditions in their fields, IRIS films could be a much more practical option than other more expensive and labor-intensive techniques like porewater sampling and the use of multiple redox probes. We have shown that IRIS films would give farmers and researchers a clearer picture of the reducing conditions in their fields and for that reasons, IRIS films may be a great addition for management of AWD despite the heterogeneity of soil.

While management of AWD may be difficult because of the heterogeneity of soil, IRIS films make it possible to understand the severity of reductive dissolution of the Fe oxides that drive As release to porewater. Because of this, we believe IRIS films are a
better tool for AWD management than current water measurement wells that might not represent actual soil reducing conditions and expensive redox probes that give only the electrochemical capacity for reduction rather than actual reduction rates. For these reasons, IRIS films should be further evaluated as a low-cost tool for farmers to use an indicator of reducing conditions in rice paddies.
Chapter 3

CONSIDERATIONS FOR IRIS FILM IMPLEMENTATION

Introduction

Arsenic (As) is a toxic metalloid that is naturally available in many soil environments but is not essential for life\textsuperscript{1,2}. Arsenic accumulation in rice grain is a human health concern that is worsened by the conventional flooded conditions typically used in rice production\textsuperscript{38}. Alternate wetting and drying (AWD) can decrease As uptake in rice when managed carefully to allow the precipitation of iron (Fe) and manganese (Mn) oxides that bind As in the soil\textsuperscript{57,59,61,62}. However, management of AWD in order to decrease As mobility in soil has proven difficult due to diverse hydrologic and soil conditions from field to field\textsuperscript{70,81}. Current management techniques of AWD can decrease water use and greenhouse gas emissions, but the ability to decrease As uptake in rice is not consistent and tends to rely on the severity or length of the drying cycles\textsuperscript{57,62,64}. Because reducing conditions in the soil drive the release of As from Fe and Mn oxy(hyd)roxides through reductive dissolution, soil Eh is an effective indicator of the conditions that promote the release of As to porewater\textsuperscript{82}. Typically, Eh is measured using platinum electrodes and expensive equipment, which is not available to rice farmers in developing countries where As in rice is a major health concern\textsuperscript{85}. Farmers need a
low-cost tool to monitor reducing conditions in their rice fields in order to better manage AWD. In addition of farmers, researchers who wish to understand spatial variability of reducing conditions in their fields need a low-cost tool that could be utilized in the place of multiple redox probes or extensive porewater sampling. Therefore, we propose that Indicator of Redox in Soil (IRIS) films could serve as a passive sensor that farmers and researchers could use to identify the reducing conditions that lead to As mobility in soil. The information farmers gain form IRIS films could help inform the management of AWD and decrease uptake of As by rice plants. While we have shown the effectiveness of IRIS films to indicate reducing conditions in rice paddies, there is still a question of feasibility and implementation, especially in developing countries.

Implementing a new agricultural technology can be difficult under any circumstance, but this is especially true in the developing world where agriculture is the main source of income for a large majority of households\textsuperscript{115}. Many factors must align for farmers in the developing world to adopt new technologies. Policy makers are integral to the process and must consider all the factors at hand including knowledge gaps, technology transfer, available infrastructure, intellectual property rights, and willingness to adopt new technologies\textsuperscript{116}. Additionally, implementation of new technologies requires collaboration with local governments and stakeholders, non-government institutions, universities, and most importantly, people\textsuperscript{116}. Here, we will explore some key factors of implementing new agricultural technologies focusing mostly on the developing world. We will discuss some of the limiting factors and barriers to implementation, especially as it relates to AWD and the IRIS technology. We believe it is important to explore the
barriers and possible strategies of implementation despite the fact that more work is needed to understand the use of IRIS in rice paddies to monitor AWD management.

**Technology and Knowledge Transfer**

In the development context, technology has many definitions that do not necessarily translate to the transfer of material goods from person to person, but rather the transfer of knowledge that may lead to the adoption or acquisition of goods, materials or tools\textsuperscript{116}. IRIS films themselves are a material good or technology, but as we have demonstrated, a certain level of knowledge is needed to deploy, retrieve, analyze, and interpret the data they provide. These factors make the implementation of IRIS films a difficult and complicated task because knowledge transfer is challenging and does not always result in significant levels of technology adoption and retention. Some studies on the adoption of AWD have shown that there must be a certain level of organizational willingness that some knowledge dissemination programs do not have\textsuperscript{117,118}. While local programs managed mostly by both agricultural extension programs and non-government organizations (NGOs) have had success implementing AWD with repetitive trainings and participatory programs, larger programs that only implement things like radio broadcasts and text alert type systems do not have as much success in adoption of AWD\textsuperscript{117,119}. These low rates of adoption could be due to knowledge gaps surrounding these forms of communication and access to technology in rural areas\textsuperscript{117,119}.
**Important Factors Influencing AWD Adoption**

Because the use of IRIS films for AWD is dependent on the adoption of AWD, it is important to understand the dynamics of the adoption of AWD in some regions. Factors like profitability, farm sizes, access to and control of irrigation, weed management, enhancement of social capital, and climate are just some of the factors limiting the adoption of AWD\textsuperscript{117,118,120,121}.

A study that examined the adoption of AWD by farmer-cooperators across the Philippines found that AWD decreased water use by 15-30%, had no effect on or even increased yield, and decreased fuel consumption by up to 40\%\textsuperscript{120}. These combined factors led to increased net return (up to a 25\% increase) mostly due to fuel cost of pumping water from deep well systems farmers use in that region\textsuperscript{120}. Despite the proven benefits, success of AWD adoption in this region was limited by key factors including collective farming group sizes and size of their service area, institutional linkages, and the enhancement of social capital\textsuperscript{120}. The success of AWD in the Philippines was highly linked to partnerships between the International Rice Research Institute (IRRI), local government officials, and particularly the National Irrigation Administration (NIA) and the Philippine Rice Research Institute (PhilRice). These organization held extensive trainings and extension activities and partnered with many institutions and universities. These efforts ensured that appropriate knowledge and information about AWD was received by farmers and had a large effect on the adoption of AWD as nearly 80\% of the farmers surveyed after training activities believed that less water throughout the growing season was not bad for the rice crop\textsuperscript{120}. 
Weed Management

As previously noted, some researchers have reported an increase in weed growth under AWD. Weed growth is inhibited when water is consistently covering soil in conventional flooded production (continuous flooding), but AWD allows the soil to dry enough that weeds are able to establish\textsuperscript{118,119}. The establishment of weeds during dry periods of AWD can increase labor and chemical costs. Plus, management of weeds must be swift in order to minimize the possible effect of weed growth on rice yield reduction\textsuperscript{116}. If the establishment of weeds is handled early, the extra cost of labor is offset by savings in water use and possible increase in yield\textsuperscript{118,119}.

Economic Incentive to Behavior Change

Perhaps the most limiting factor to the adoption of AWD is motivation or economic incentive to decrease water use. A study done on AWD in Nepal found that although AWD was successful in reducing water use by an average of 57\% without seeing a decrease in crop yield, surveyed farmers were reluctant to say that they would adopt AWD as their main irrigation technique primarily. This reluctance stems from the fact that a lot of farmers in Nepal pay for water by land area rather than volume of water used\textsuperscript{73}. Similarly, in Bangladesh most farmers do not own their own irrigation pump. The 2008 census in Bangladesh revealed that only 2\% of the sampled rural households (814,058 households) owned their irrigation pump\textsuperscript{121}. As such, a majority of farmers must rely on pump owners or farmer cooperatives to obtain irrigation water and farmers are mostly charged fixed rates based on land area rather than volume of water used.
In scenarios where farmers pay for water by land area, only the pump owner benefits from the decrease in water use for production. In Bangladesh, this disparity led extension agents from a USAID funded Cereal System Initiative for South Asia (CSISA) to communicate directly with pump owners and devise a plan for the implementation of AWD in order to increase profit for pump owners\textsuperscript{117}. Pump owners began charging farmers for the water they pumped on an hourly basis, which encouraged the use of AWD and freed up time and water availability so much that pump owners were able to extend their reach to more farmers\textsuperscript{117}. In this case, the implementation of AWD was beneficial for the pump owners and the farmers. However, when a NGO, (Rangpur Dinajpur Rural Service or RDRS) tried to use the same strategy in different communities, pump owners who were using government subsidized electricity were unwilling to change their practices because they did not see as much of a decrease in the cost of running the irrigation pumps\textsuperscript{117}. This outcome suggests that pump owners are highly motivated by their profit margin and what works in one community may not work in another.

*Current Tools for AWD Management*

While knowledge transfer is the main concern for the adoption of AWD, water measurement wells referenced early in this work are a tangible component of AWD systems that are required for successful adoption. Water management wells must be distributed or made with local materials that are available to farmers which can be difficult because there must be a mode of distribution or access to appropriate materials. The International Rice Research Institute (IRRI) has educated many farmers about the use of water measurement wells\textsuperscript{63}, but NGOs and private stakeholders are also involved.
For instance, Syngenta, a agrochemical and seed company based in Switzerland has distributed water measurement wells made of PVC to farmers that are using their products for rice production\textsuperscript{119}. Other farmers who do not have access to PVC pipe or similar material make their own water measurement wells using plastic bottles or bamboo\textsuperscript{67,119}.

AWD works best in fields that have been adequately leveled to ensure uniform drying of the whole paddy\textsuperscript{67}. However, this is not always the case and farmers must monitor areas that are high spots in the field to ensure the crop is not going to be damaged by over drying. Water measurement wells only allow the farmer to monitor the water level in one small location of the field. Farmers must make a field scale decision when managing AWD, which is difficult using only water management wells. This is where IRIS films could be a crucial decision support tool for farmers implementing AWD.

\textbf{Important Factors for Possible IRIS Film Adoption}

While AWD is a complex system that holds its own challenges, the additional use of IRIS films to manage AWD would be a valuable asset for farmers who must make field scale decisions on irrigation management. However, IRIS films do introduce further challenges to the dissemination of knowledge and the distribution of required materials necessary for their use on the field scale. Because farmers who are in control of irrigation practices tend only to adopt AWD when they have an economic incentive, the addition of
IRIS films may not be appealing for most farmers because the IRIS films represent another input that would cut into their net profit. Even though IRIS films are a much more cost-effective tool to understand redox processes, farmers may not understand or value the advantage that they possess.

Scale, Knowledge Transfer, and Pilot Programs

IRIS films, while much less expensive than traditional measures of Eh are not currently produced on a scale that would be affordable for farmers. In order for the implementation of IRIS films to work, local sources would have to be available to make them affordable for farmers in the developing world. Especially considering farmers would need to install sets of 3-4 films in multiple field locations per flooding period. It may not be cost effective to implement IRIS films without the aid of organizations that have the infrastructure for producing films and a known pathway for knowledge transfer that is local and targets farmers individually as local strategies have worked for similar groups in the past\textsuperscript{117,119}. Because of this, we believe that implementation of IRIS films to monitor AWD management would need to be facilitated through local governments or educational and research institutions, especially those that are concerned with As consumption in specific countries.

Additionally, implementation of IRIS films would not be possible without the widespread use of AWD. In the future, a possible pilot location for the implementation of the IRIS technology might be a nation like Bangladesh, where AWD is already somewhat established as a water management technique that works. While adoption of AWD may still be low, many agencies are already working to extend AWD in Bangladesh\textsuperscript{117}. By
gaining support of these organizations, much of the infrastructure and knowledge sharing pathways would already be in place. Additionally, as previously discussed, As exposure is already a major concern in Bangladesh\textsuperscript{19,20}, which may be a strong motivator for the adoption of the IRIS technology.

*Perceived Usefulness and Ease of Use*

In addition to the importance of economic benefit to the adoption of new technologies, the perception of the technology is just as important. The Technology Acceptance Model (TAM) is a theoretical model to help explain the motivation behind the adoption of new technologies. A study that used TAM to evaluate the adoption of precision agriculture techniques found that while increased profitability is the main motivation for the use of new technologies, belief that the new technology is useful is also a major factor in adoption\textsuperscript{122}. Researchers studying the adoption of precision agriculture tools have found that usefulness and ease of use are main factors in the adoption of precision agriculture technologies\textsuperscript{122,123}. Perceived usefulness is the amount a person might think a particular technology or system would enhance their job performance or that they would be able to use the technology advantageously\textsuperscript{124}. Perceived ease of use is the degree that a person believes the technology or system could be used easily or without considerable effort\textsuperscript{124}. It could be argued that farmers who know the health implications of As accumulation in rice grain might be more willing to adopt the use of IRIS films in AWD management because they would understand the usefulness of the technology for the health of their families. In contrast, farmers who
might not be knowledgeable about As in rice grain might favor the current management practices of AWD and see IRIS films an unnecessary management tool.

*IRIS Film Analysis Tools*

A limiting factor that might hinder the acceptance of the IRIS technology by farmers is ease of use. While the deployment process for IRIS films is simple and in field demonstrations by trained professionals would most likely be sufficient based on previous work\textsuperscript{119,123,125} the analysis and interpretation of IRIS films brings about its own challenges. As previously described, there are methods of analysis and interpretation for IRIS films: (i) the visual assessment method, which is unreliable and extremely subjective\textsuperscript{97}, (ii) the grid method of quantification which is reliable but extremely time consuming and still subjective,\textsuperscript{101} and (iii) the image analysis method, which is the least subjective but requires expensive equipment and is still quite time consuming\textsuperscript{89,98–100}.

We developed a program called IRIS Imager that is comparable to other methods of quantification but removes subjectivity and is not as time consuming as other methods. It does, however, require expensive equipment and MATLAB software, both of which are not readily available in developing nations and could not be used in the field. This barrier to implementation could perhaps be overcome by the development of a mobile application (app) that would take the IRIS Imager code and make it available offline on mobile devices.

Due to the rapid growth of mobile phone usage worldwide (especially in developing countries), mobile applications allow for information exchange in rural areas that otherwise have a hard time receiving information\textsuperscript{126}. A mobile app would allow
farmers with access to a smart phone the ability to take a picture of the IRIS film in the IRIS Imager app and quickly retrieve accurate and objective IRIS paint removal percentages. Farmers without access to a mobile phone could be trained on the use of the grid method as it has been shown to be effective previously and by our study\textsuperscript{101}. While a mobile app is not a tangible product at this time, we have begun discussing a patent for IRIS Imager and a subsequent mobile application. We believe a mobile app of IRIS Imager would aid in the implementation of the IRIS film technology and the dissemination of knowledge that goes along with it.

Much work would need to be done to understand the use of IRIS films in rice paddies to monitor AWD management in order to extend the technology to real farmers. While in my work I studied spatial variability in rice paddy mesocosms, field scale studies would need to take place to understand the spatial variability across rice paddies. Only then could more accurate and quantitative recommendations for the deployment and analysis of IRIS films be made to inform decisions about AWD management.

**IRIS Film Implementation Study Using GIS**

Because of the many unknowns surrounding IRIS film implementation, a possible course of action could be to implement a pilot study in a country that meets specific criteria. In order to do this, a GIS Study was conducted to visualize possible pilot nations. Three criteria were used to evaluate different nations: (i) paddy rice production, (ii) higher than normal soil and groundwater As content, and (iii) presence of three different
international aid organizations. Rice production was a key criterion because paddy rice production is necessary for the use of AWD. Additionally, we sought nations that have reported high As content in soils because decreasing As uptake in rice grain is the main driver for the use of IRIS films in rice paddies. The international aid organizations chosen were the World Food Program (WFP), United States Agency for International Development (USAID) and The United States Peace Corps. Presence of these aid organizations was chosen because previous work has shown that smaller trainings and in person contact is a more sustainable strategy for implementation\textsuperscript{117,119}. Plus, these organizations are known to focus efforts on either agriculture, human health, or both\textsuperscript{127–129}. Additionally, these organizations often partner with local governments, research institutions, and NGOs to help on the ground in remote rural areas\textsuperscript{127–129}.

Data Collection, Visualization and Analysis

Rice production data was compiled from the Food and Agriculture Organization of the United Nations (FAO) Rice Market Monitor for 2017 production and reported in tons of rice produced\textsuperscript{130}. Soil and groundwater As data was compiled from multiple sources\textsuperscript{6,131}. Presence of WFP, USAID, and Peace Corps in countries was compiled from their respective annual reports from 2017 or their respective webpages\textsuperscript{132–134}.

Data was transferred to geographic information system (GIS) software (Esri - ArcGIS Pro 2.4) where it was joined to a country boundaries shapefile. Countries with rice production were symbolized using graduated colors based on paddy production in tons. Countries with higher than normal As in soil and groundwater were denoted using single symbols and presence of aid organizations was symbolized using graduated
symbols (Figure 3.1). Analysis was done in three phases and select by attribute was used to highlight countries based on their selection criteria. Phase 1 selected countries with the highest rice production values (> 100 million tonnes), recorded high As levels concentrations and the presence of three aid organizations. Phase 2 selected countries with the highest rice production values (> 100 million tonnes), recorded high As concentrations and presence of at least 2 aid organizations. Lastly, Phase 3 selected countries with moderately high rice production (> 50 million tonnes), reported high As concentrations and presence of at least two aid organizations.

Figure 3.1: The IRIS film pilot implementation study was conducted to identify counties that might be considered for pilot implementation programs if IRIS were to be implemented as a tool to monitor AWD in rice paddies. Rice production (millions of tonnes) is denoted with in green, countries with reported widespread As contamination are demoted with a white star, and the number of the three aid organizations a country has is denoted by a pink, orange or red circle.
Results and Implications

Based on the selection criteria outlined above, four nations were identified as possible pilot nations: China (Phase 1) (Figure 3.2), India (Phase 2) (Figure 3.3) Bangladesh and Indonesia (Phase 3) (Figure 3.4). While many other factors must be considered, this does provide a base for further study. Selection criteria could be modified to include countries with lower levels of rice production like Cambodia and Thailand, or countries with fewer aid organizations like Vietnam. Additionally, further study would require analysis of social and political climate, access to technology, availability and use of controlled irrigation systems, current use of AWD and willingness to try new technologies like AWD and IRIS films. After considering these additional factors, the pilot nations identified may shift. More research would need to be conducted to fully understand how IRIS can be used to monitor AWD in rice paddies. As we gain more knowledge and improve upon quantification and analysis, implementation strategies could be tailored to promote the use of IRIS films in the best way possible.
Figure 3.2: Phase 1 indicates that China is the only country with the highest rice production (>100 million tonnes), reported widespread As contamination and the presence of all three selected aid organizations.

Figure 3.3: Phase 2 indicates that China and India are the only countries with the highest rice production (>100 million tonnes), reported widespread As contamination, and the presence of at least two of the three selected aid organizations.
Figure 3.4: Phase 3 indicates that China, India, Bangladesh, and Indonesia are the only countries with high rice production (>50 million tonnes), reported widespread As concentrations, and the presence of at least two of the three selected aid organizations.

*IRIS Films for Rice Research*

As we have shown, IRIS film implementation in the developing world, though not impossible, would not be easy. Perhaps a more realistic use for IRIS films in rice paddies at this time would be by researchers wanting to understand the spatial variability of reducing conditions in their rice fields. Rather than installing multiple redox probes at different depths all over a field, IRIS films could give researchers a visual tool to assess the variability of reducing conditions in a wide range of field conditions and management strategies. Researchers generally have access to more funds and have the knowledge base to adapt the technology to their needs. Adoption strategies mentioned here, such as a
mobile app for IRIS film analysis, could still be very beneficial for researchers, especially those using IRIS films on a large field scale.
REFERENCES


(11) EPA. Exposure and Risk Assessment for Arsenic; 1982; Vol. PB85221711.


(15) CGWB. *High Incidence of Arsenic in Groundwater in West Bengal*; 1999.


(63) FAO. Rice Farming: Saving Water through Alternate Wetting Climate Change Adaptation and Disaster Risk Reduction. 2013, 1–3.


(86) Jenkinson, B. J. Hydrology of Sandy Soils in Northwest Indiana and Iron Oxide Indicators to Identify Hydric Soils, Purdue University, Thesis, 2002.


(118) Rahman, S. M. Case Studies of Farmers’ Perceptions and Potential of Alternate Wetting and Drying (AWD) in Two Districts of Bangladesh. 2016.


(126) Qiang, C. Z.; Kuek, S. C.; Dymond, A.; Esselaar, S. Mobile Applications for Agriculture and Rural Development. **2011**.

(127) WFP. *World Food Programme: Overview*; 2019.


(132) World Food Programme. *Where We Work*.

