Guixi Rice Paddy Remediation Pilot Study

Jianxi Province, China

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I. Introduction

Blacksmith Institute is working with the Jiangxi Academy of Environmental Sciences and the Guixi Environmental Protection Bureau to stop endemic lead poisoning and remove other heavy metals from one of the largest copper smelters in China. This work is conducting a risk assessment and testing soil remediation strategies in one of the most highly affected residential areas – ShuiDuiQuan Village.

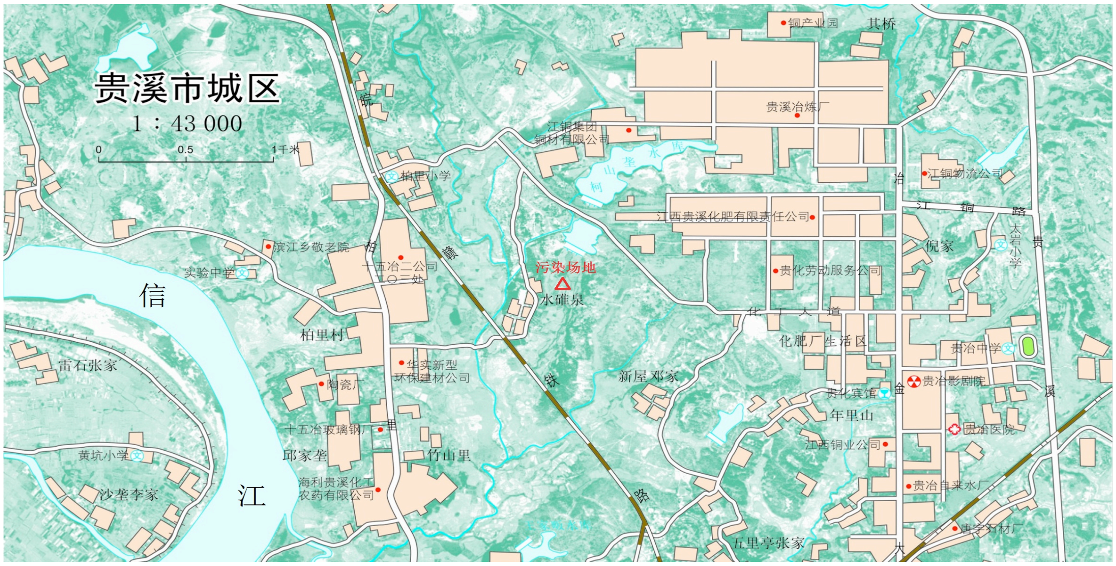
The purpose of this project is to demonstrate technically and economically viable methods to remediate agricultural land, in particular rice paddies, contaminated with cadmium, copper, and arsenic in Guixi, Jiangxi Province. The contamination is due to heavy metal releases from a large copper smelter in Guixi. These releases were both to the atmosphere, resulting in deposition on the rice paddies, and into water used for rice paddy irrigation. The desired goal is to be able to restore the paddies sufficiently that they can return to agricultural use for food crops. The minimum goal is to remediate the land to meet the standard for urban land utilization and eliminate the risk of direct impact to human health and the environment.

II. Background

The Guixi Smelter is the largest copper-smelting factory in China. It was established at the beginning of the 1980's and contributes greatly to the local economy. However, it also has discharged significant pollution to the local environment, particularly metals (copper, cadmium, arsenic, lead and others) and acid gases (SO_2 and H_2SO_4). Fifteen 15 villages with a total population of 10,000 people are affected. The affected rice farmland area has been estimated at 132 hectares and vegetable farmland at 6 hectares.

Guixi City is located in the Northeast of Jiangxi province, along the Xinjiang River. The geology is cretaceous red sandstone with little groundwater. The ground water is mainly born in the soil, being perched and phreatic groundwater. The soil in the area and in particular, the project area, is red soil and paddy soil.

The pilot project is locted adjacent to ShuiDuiQuan village, one of the severely polluted areas, southwest and directly downwind (in the prevailing wind direction) of the smelter factory. Water in the area formerly came from the Keshalong reservoir, which serves as a cooling and wastewater discharge point for the smelter, but now discharges from this reservoir are diverted around the project area via a canal and are discharged directly to the Xinjiang River. The project area now receives water from a smaller reservoir constructed below the Keshalong reservoir, which does not receive direct discharges from the smelter, although it may receive contaminated discharges from contaminated soil, surface runoff and several small other industrial sources. The project area was formerly used for wetland rice, but is now unused, although there are small fields in the area used for vegetables and a few rice paddies are still in use nearby. There are three (3) ditches from the lower reservoir to the village for the purpose of irrigation.



Map: Location of the pilot project site (Marked by red triangle)

The project area soil is heavily contaminated with cadmium, copper, arsenic, and to a lesser extent lead. There has been extensive sampling. The worst contamination is related to cadmium, for which all soil samples were over the agricultural standard of 0.3 mg/kg, sometimes over by a factor of 10 or more. Water samples in the project area were tested and were over the irrigation water standards for arsenic and cadmium, with the arsenic levels being the worst. Rice grown in the area was also tested, with a result that 100% of samples were over the cadmium standard, and 37% of the samples were over the lead standard, though only one sample showed a small exceedence for arsenic. Full sample results and sample locations are provided in the project proposal documents.

Appendix 1 shows an aerial map of Guixi. Appendix 2 shows a more detailed map of the project site, including where sampling took place. Appendix 3 shows a sketch of the two plots within the project site as well as sampling depths.

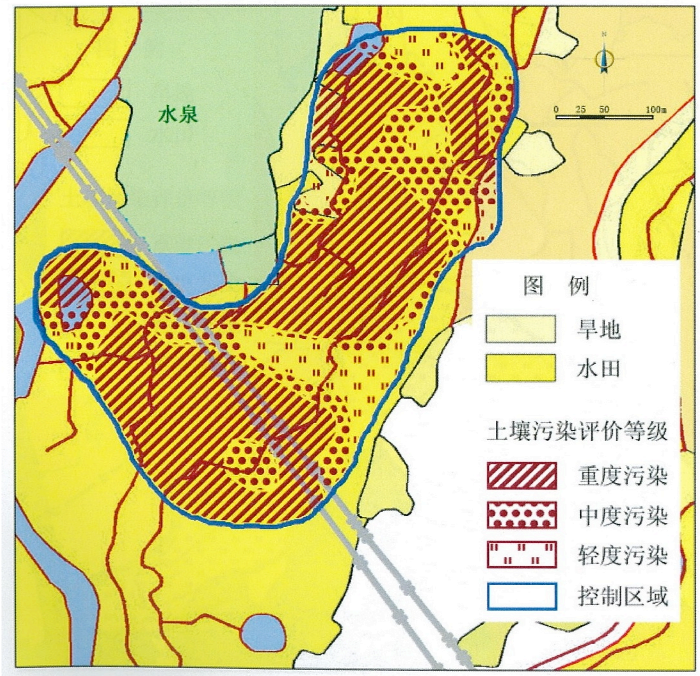


Fig 3 The use of land and the pollution status of the metal, Cd

III. Remediation and Land Restoration Strategy

The recommended overall strategy to remediate the site is fix the cadmium into the rice paddy soil such that it 1) it will not significantly migrate or leach to groundwater and 2) is largely unavailable to be taken up by rice (or vegetable) plants. This would be accomplished by adjusting the soil pH and adding amendments (stabilizers and chemicals) to fix the cadmium. The key environmental and public health concern is the cadmium, which is toxic at very low concentrations and as testing has shown, is the primary contaminant absorbed by the rice, present far over pollution-free standards in all rice samples taken. It is also well over agricultural standards in all soil samples and in 40% of the water samples in the project area.

Other metals of potential concern are copper, lead and arsenic. Copper is over soil standards for most soil samples, but not over water standards. However public health impacts are not considered very significant for copper soil contamination, and uptake into rice does not present a similar level of risk to that of cadmium. Lead, while present, has been found to be mostly below standards in the soil and rice, and always below the standard in the water. The fixation technology to be used for cadmium will also tend to fix lead and copper as well.

Regarding arsenic, 37% of soil samples in the project area were over the agricultural standard of 30 mg/kg, and 100% of water samples were over the irrigation water standard of 50 µg/l, sometimes by a factor of 7. However, the sampling was performed in 2007, and since then levels of arsenic may have changed significantly.

Furthermore, the diversion of effluent from the Keshalong reservoir directly to the Xinjiang River, bypassing the project area, should have resulted in elimination or great reduction in new arsenic loading to the project area. Since arsenic is soluble in water, if there is no significant new loading, arsenic levels in the soil and groundwater should naturally attenuate, particularly in view of the high levels of rainfall in the area (estimated at 1,800 mm/year). Also, arsenic levels in the rice grown in the project area were below the standard for pollution-free rice (0.5 mg/kg) in all but one of nineteen (19) samples, and the one exceedence was only at 0.6 mg/kg. A re-sampling of rice samples,could show lower levels due to natural attenuation. Before any decision is made to address arsenic in remediation planning, further samples should be gathered of the water now available for irrigation in the project area, as well as current levels in soil. Blacksmith considers it likely that testing will show that arsenic is not presenting a public health risk for the intended use of the area (agricultural) or to people in the area, and so remediation may not be necessary. If arsenic is still present above standards, investigation needs to be performed to determine the continuing origin. In particular, potential sources feeding into the current small reservoir upstream of the project area, would have to be investigated.

Another possible remediation strategy, phytoremediation, is not recommended to be tried for the pilot project. The primary reason for this is that phytoremediation is already being piloted by the Guixi city government at a contaminated location northeast of the copper smelter. Secondly, successful phytoremediation demostration would take far longer (*i.e.,* multiple years) than anticipated for this project (which is planned to conclude by June, 2013. Lastly, the funds available for this project will be completely consumed by testing fixation.

IV. Test Plot Preparation for the Pilot Test Project

Within the project area, it is proposed that two (2) plots roughly the size of a single rice paddy field as distinguished by the earthen berms that define the fields, be selected. These plots should be drained to the extent practical. The Plots should be cleared of any residual plantings that may add additional heavy metal impacts and/or nutrients to the soil as the plant material continues to decay. The rough location of the test plots is shown on Appendix 2. Appendix 3 gives a sketch of the test plots and soil sampling depths.

The plan is to treat Plot I with a pH amendment with a capacity that allows for residual buffering through a planting season. A second plot will receive both pH adjustment and a soil amendment intended to assist in “fixing” cadmium specifically, and other heavy metals generally. Specific chemicals and application amounts will be determined once soil testing in the test plots is complete as per Section 5 below. The chemicals and application rates are highly dependent upon natural soil conditions.

Once the soil testing is accomplished, recommendations will also be provided regarding methods to mix chemicals into the soil, and depths required for mixing.

V. Soil Testing

In order to conduct the site remediation project, additional information will be needed to both assess the soil structure and chemical composition. Samples for the general list and specific list of parameters below should be gathered at the root zone depth, and a second sample at a depth of 1 meter, or where the soil lithology indicates a distinct change in soil characteristics inferring a larger fraction of organic carbon buildup or a finer-grained material. A sampling location (that includes the two referenced depths) should be chosen in each of the paddy fields such that each field is triangulated by three (3) locations (see attached sketch).

General Soil Characterization List	**US Method**
Unified Soil Classification System	ASTM D2487
Particle (Grain) Size	ASTM D422
Sieve Analysis of Fine and Coarse Aggregates	ASTM C136 - 06
Total Organic Carbon (Water)	EPA 415.1 or 415.2
Total Organic Carbon (Soil)	SW 846 Modified 9060
Dissolved Organic Carbon (Water)	0.45 μm filter, then EPA 415.1 or 415.2
Soil pH	SW 846 9045c or ASTM D4972
Groundwater pH	EPA 150.1
Cation Exchange capacity (CEC)	EPA 9081
Soil Moisture	ASTM D2216
Atterberg Limits (LL, PL, PI)	ASTM D4318
Total Iron	SW 846 6020
Total Manganese (Soil)	Digest SW 846 3050B, 3051 or 3052 Analyses SW 846 7460, 6010B, or 6020

In order to recommend potential soil additives that may assist in “fixing” these heavy metal contaminants in soil, rendering them unavailable for biological uptake, we also need to establish a baseline for determining the agricultural viability of the fields as they exist now. Thus, we would also like analysis for the following nutrients essential to rice cultivation.

Soil Nutrients Test List	**US Method**
Total Iron (Fe)	SW 846 6020
Nitrogen (N) as Ammonia	EPA 350.1
Nitrogen (N) as Nitrate-Nitrite	EPA 353.2
Nitrogen (N) as TKN	EPA 351.1
Phosphorous (P)	EPA 365.4
Potassium (K)	Mehlich-3 soil test method
Zinc (Zn)	SW 846 6020
Sulfur (S)	EPA 6010

Finally, we would like further analysis of the contaminants themselves. Therefore, the soil samples should be evaluated for the presence of:

Soil Contaminants Test List (Total and SPLP)	**US Method**
Copper (Cu)	SW 846 6020 and EPA 1312 (SPLP)
Arsenic (As)	SW 846 6020 and EPA 1312 (SPLP)
Cadmium (Cd)	SW 846 6020 and EPA 1312 (SPLP)
Lead (Pb)	SW 846 6020 and EPA 1312 (SPLP)
Mercury (Hg)	SW 846 7471

VI. Water Testing

As discussed in section 3 above regarding arsenic, further testing of water used as a source for irrigation in the project area is needed. Suggested sampling locations are shown on Appendix 2 and are described below:

- At the outfall of the small new reservoir the forms the headwaters of the irrigation water source for the project area; and

- In the irrigation water supply stream upstream but reasonably near the project area, such as 100 meters upstream from the test plots

Sediments should also be tested at these two locations, at the bottom of the stream in an area similar to the surface water sampling. In addition, sediments should be tested from the bottom of what appears to be, on aerial photographs, a small pond or swampy area of the stream roughly 100 meters downstream of the reservoir dam. The purpose of the sediment sampling is to determine if sediments can be a continuing source of heavy metal contamination of the water due to past discharges, particularly for arsenic.

The water samples should be tested for the following parameters:

Irrigation Water And Contaminants Sediment Contaminant Test List	**US Method**
pH	SW 846 9045c or ASTM D4972
Copper (Cu)	SW 846 6020 and EPA 1312 (SPLP)
Arsenic (As)	SW 846 6020 and EPA 1312 (SPLP)
Cadmium (Cd)	SW 846 6020 and EPA 1312 (SPLP)
Lead (Pb)	SW 846 6020 and EPA 1312 (SPLP)
Mercury (Hg)	SW 846 7471

Appendix

Appendix 1

To see all the details that are visible on the screen, use the "Print" link next to the map.

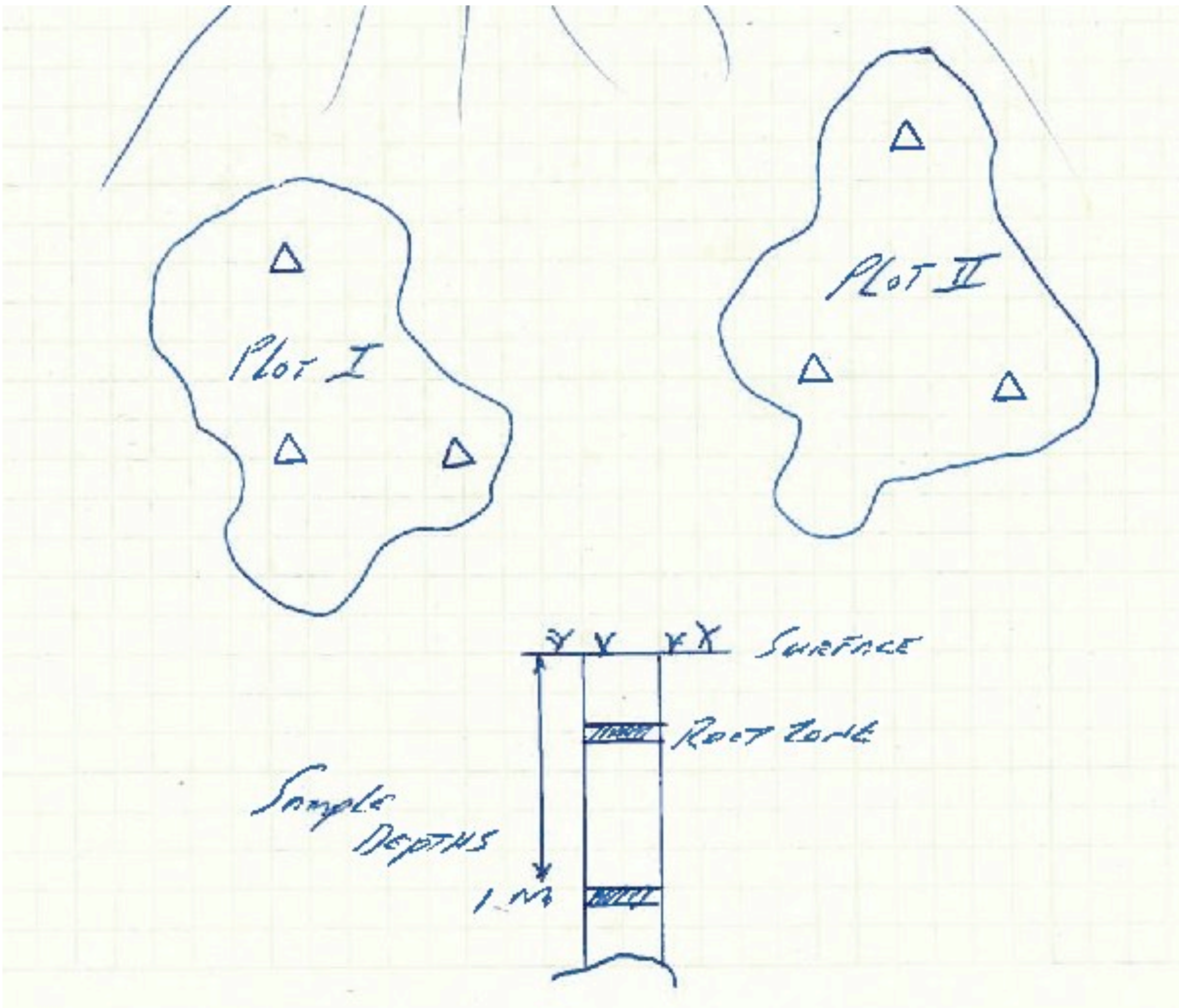
Appendix 2

To see all the details that are visible on the screen, use the "Print" link next to the map.

Google

Appendix 3

Test Plot Diagram



Appendix 4

Soil Amendment Protocol

Based on the data obtained through site testing, it is proposed that both pilot plots receive the application of lime for pH adjustment. The volume of application should consist of approximately 3 – 4 tons per acre, and be disced into the upper 15 – 20 centimeters of the tests plots after the draining of excess surface water. Following lime treatment, one of the two pilot plots should receive the addition of a secondary soil amendment, largely consisting of the byproduct of wheat milling and the addition of zero-valent iron. We have identified a proprietary product (DARAMEND®) that can be acquired in the United States and shipped to China. However, it may be possible to identify a suitable substitute within China to assist in cost economy and thereby maximize the monies available for actual site improvement.

The DARAMEND® product is designed to quantify the potential of the combined action of E_h and pH adjustment to reduce the availability of the heavy metal contaminants at the site to satisfactory levels for cultivation. DARAMEND® is a specially formulated metal remediation compound for in situ immobilization of soluble metals via enhanced precipitation and adsorption. Reduction potential (also known as redox potential, oxidation/reduction potential, ORP or E_h) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. The heavy metal, cadmium, will be specifically receptive to this treatment.

While the selection of the product in this instance is to reduce the concentrations of heavy metals (specifically cadmium) within the upper soil regime, the product has been used to treat soils containing metals, chlorinated herbicides and pesticides, organic explosive compounds, and chlorinated volatile organic compounds (CVOCs), and thus its successful application in this instance, may have far reaching applicability for other contaminants and contaminated sites throughout China.

Beyond the selection of this product based on its ingredients and ability to “fix” cadmium within soils, this product is uniquely advantageous because: i) it can be applied with standard agricultural procedures, such as through discing, ii) its implementation generates no odors or leachate, and iii) it can be applied in a reasonably small quantity (*i.e.,* weight to soil mass) to achieve the desired results.

From a sustainability perspective, this application offers many benefits over “dig-and-dump” approaches. Furthermore, proper application offers accelerated treatment and yields shorter remediation schedules as compared to traditional bioremediation processes.

We are also impressed with the controlled-release feature of the carbon, which provides for extended longevity and greatly assists in maintaining very low redox conditions through simultaneous microbial consumption of the carbon and electron acceptors. Cadmium, for example, will precipitate with sulfides, following stimulated heterotrophic microbial sulfate reduction to sulfide. Adsorption to iron corrosion products (*e.g.* – iron oxides and oxyhydroxides) promotes precipitation through the production of iron cadmium sulfide minerals that are practically insoluble in groundwater. These processes will reduce the availability of the cadmium to the crop plants and also lessen the leaching of Cadmium farther through the soil profile.

For the Guixi Rice Paddy remediation pilot study, it is recommended that the pilot plots be drained prior to any amendment with lime or the DARAMEND® product. The plot receiving the secondary DARAMEND® product amendment should be split into thirds. The product should be disced into the upper 15 centimeters of the soil column at a rate of 0.5%, 0.1%, and 0.01%, equating to 14,500, 2,900, and 290 kg per hectare, respectively.

For reference, typical environmental application rates of the DARAMEND® product for ex situ treatment of soil range from 1% to 3% by weight for organic contaminants, but the application rate may be substantially reduced for successful metals treatment, especially considering that the primary purpose of such treatment is NOT to cleanup up the soil per se, rather preclude substantial uptake of cadmium by the rice crop.

The successful application of the DARAMEND® product will require uniform distribution within the treatment zone, and hydration of the soil during the treatment cycles. The optimum pilot test design would include selection of distinct zones within the total test plot and treatment with the product application rates of 0.5%, 0.1% and 0.01% followed by post-treatment sampling to quantify the availability of the Cadmium in treated soils compared to a control section.

Finally, also recognize that product will influence the availability of other metals, which may require supplemental fertilization following treatment. Zinc, for example, is of particular concern in this respect, but can be added post treatment via traditional fertilizer application, as a seed treatment or as a foliar chelate in the seedling stage.