# Washington University in St. Louis

# Investigating the Relationship between Manganese Reactivity and Arsenic Adsorption Capacity of Pleistocene Sediments from Southeast Asia

#### Introduction

Arsenic (As) contamination of well water is a major threat to human health across the globe. In Southeast Asia specifically, over 120 million people drink water naturally contaminated with dangerous As concentrations.<sup>1</sup> Increased withdrawals of As-contaminated groundwater have prompted a search for signals showing that an aquifer is at risk of dangerous concentrations of As.

This study focused on allogenic As, which is the As in groundwater pulled from an area with a high concentration to a previously uncontaminated well. Developing a predictor for future contamination based on sediment characteristics will allow for the prevention of consumption of contaminated water.

#### Goal

The primary objective of this research was to determine if there is a correlation between the concentration of manganese (Mn) oxides and the As sorption capacity of the soil, due to the oxidation of As(III) to As(V) by **Mn.** This will hopefully lead to the use of field tests for manganese oxide concentrations as a way to predict potential for future As transport and contamination of aquifers.

#### Methods

- Six sediment cores and well cuttings were collected from a Pleistocene aquifer in Cambodia and kept anaerobically at 4°C.
- Adsorption isotherm experiments for each sediment sample were prepared by mixing soil with solutions of varying As concentrations, from 0 to 5,000 ppb, for 48 hours.
- Chemical extractions were performed on each sediment in parallel to determine the concentrations of various forms of Mn, as well as Iron (Fe) and As. Each extraction removes that form of Mn plus the more weakly bound forms. The extractions, in order of increasing strength, are:
  - Exchangeable Mn: extracted with magnesium nitrate<sup>2</sup>
  - <u>Amorphous Mn oxides</u>: extracted with hydroxylamine hydrochloride<sup>3</sup>
  - <u>Crystalline Mn oxides</u>: extracted using the Citrate-Bicarbonate-Dithionate (CBD) method<sup>4</sup>
  - <u>Total Mn</u>: extracted by EPA Method 3050B, which uses nitric acid, hydrochloric acid, and hydrogen peroxide<sup>5</sup>



Arsenic, µg/L ⊚ <10 **◎** 10 – 50 **O** >50

**Figure 1.** *Left.* Map of field site in Kandal Province, Cambodia Figure 2. Bottom Left. Sediment A (MT30, 6m) Figure 3. Bottom Center. Sediment E (ME10, 27m) Figure 4. Bottom Right. Sediment F (MT30, 21m)



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### **Arsenic Adsorption Isotherm Results**

Following arsenic adsorption isotherm experiments, resulting data were fit with both Freundlich and Isotherm models. The Freundlich model is q = $K_F C^{1/n}$ , where q is the sorbed As concentration, C is the equilibrium As concentration in solution, and K<sub>F</sub> and n are modeling constants. The Langmuir model is  $q = \frac{Q_M b_A C}{1 + b_A C}$ , where q is the sorbed As concentration, C is the equilibrium As concentration in solution,  $Q_M$  is the maximum sorption, and  $b_A$ is a modeling constant. At concentrations of As below 1000 ppb, Freundlich models were a near perfect fit to our data. Langmuir models fit better for higher As concentrations.

Sediment	Sample Location	Freundlich Parameters		Langmuir Parameters	
		K <sub>F</sub> (μg/kg)	1/n	Q <sub>M</sub> (μg/kg)	b <sub>A</sub> (L/μg)
А	MT30, 6 m	370	.626	36600	2.69E-03
В	MT20, 18 m	19.8	.808	13700	7.14E-04
С	MW10, 42 m	11.8	.746	3540	1.17E-03
D	ME10, 18 m	307	.710	51200	2.83E-03
E	ME10, 27 m	420	.673	58700	2.17E-03
F	MT20, 21 m	66.1	.682	20400	7.58E-04

#### Table 1. Isotherm Parameters



Figure 5. Comparison of Freundlich Models (curves) with Experimental Data (points)



**Figure 6.** Comparison of Langmuir Models (curves) with Experimental Data (points)

#### References

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- 2. L.M. Shuman, *Soil Science*, 1985, vol. 140., pp. 11-22
- 3. T. T. Chao, Soil Science, 1972, vol. 36., pp., 764-767
- 4. O.P. Mehra, M.L. Jackson, *Clays and Clay Minerals*, 1958, vol. 7, issue 1, pp. 317-327
- 5. EPA, Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. Revision 2, 1996.

### **Chemical Extraction Results**

With the exception of Sediment D, the extractions removed increasing amounts of Mn with successive treatments.





Figure 7. Manganese Concentrations from Each Extraction

### **Correlation of As Isotherm Model Constants and Mn Extraction Data**

A linear correlation between As sorption capacity and CBD Mn concentration was found with R<sup>2</sup> equal to .873 for Freundlich models and .930 for Langmuir models. No strong relationships could be determined between the As sorption capacity and the Mn concentrations from any other extractions.



Figure 8. As Isotherm Model Constants vs. Crystalline Mn Oxide Concentration of Sediments

The correlation between crystalline Mn oxides and As sorption capacity of sediments suggests that the CBD extraction is a useful proxy for predicting the transport potential of As into aquifers. When applying this relationship, it is important to note that at the low As concentrations found in the Pleistocene sediments and in the groundwater sampled, the Freundlich isotherm is a better fit for adsorption capacity. Additionally, the distribution of different forms of Mn is not proportional, so in order to use the correlation determined above, the concentration of crystalline Mn oxides must be determined experimentally. The results of this study should lead to further investigation into other factors that might impact As sorption capacity such as competing sorbates, particle size, and iron concentration.

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#### **Chemical Fractions of Mn in Sediments**

#### Conclusions