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A Novel Arsenic Removal Method for Water

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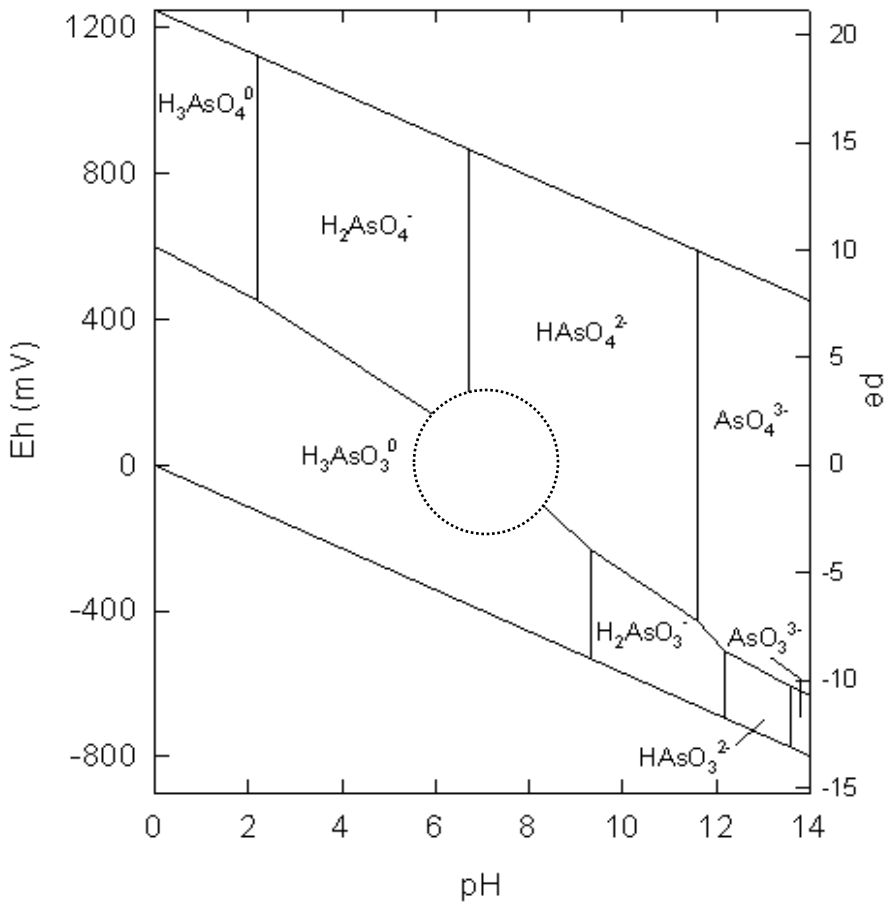
Arsenic Impacted Populations,
Bangladesh

Groundwater Arsenic Contamination Areas

Over 137 million people in more than 70 countries affected by arsenic poisoning through drinking water (Associated Press, 2007)

Background Information

- Inorganic and organic forms
- Inorganic forms include arsenite (III) and arsenate (V)
- Arsenite is more toxic than arsenate to humans
- >10 ug/L of dissolved arsenic in drinking water causes health problems (US National Research Council, 2001):
- **New arsenic Legislation for Human Drinking Water (10 ug/L) Effective from January 23, 2006 (US EPA)**



Arsenic Limits For Different Water Uses

Water Use	Arsenic Limit (µg/L or ppb)
Human Drinking Water	10
Animals	200
Agriculture	100
Fish	50

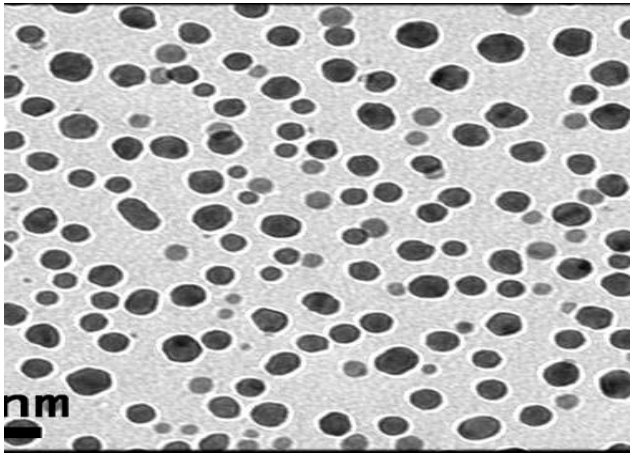
Methods to Remove Arsenic from Water

- Precipitation Process
- Adsorption Process
- Anionic Exchange Process
- Membrane Filtration Processes

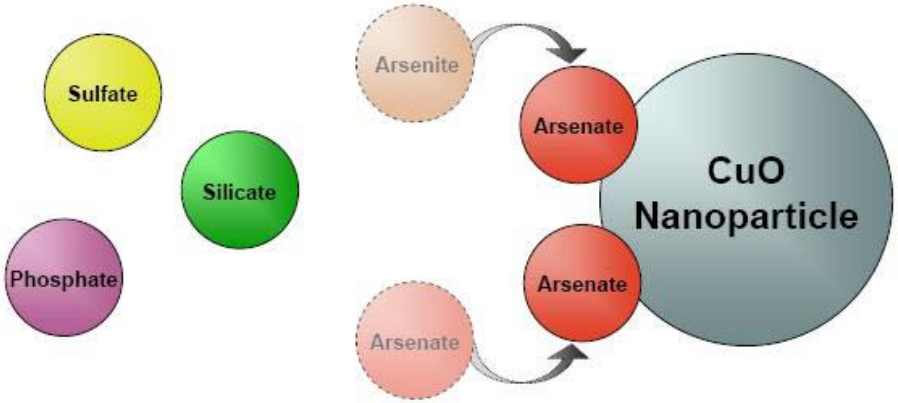
- Require oxidation step
- Require pH adjustments
- Effected by other components of water
- Not suitable for small communities and produce waste byproducts

What We Learned?

- Arsenic removal occurs rapidly under a wide-range of water chemistries without pH adjustment or preoxidation step.
- Arsenic adsorption mechanism involves oxidation of arsenic(III) to arsenic(V) on the surface of CuO particles.
- Common ions in water showed no effect in removal of arsenic by CuO particles.
- Maximum adsorption capacity 23-25mg As/g CuO. CuO particles can be regenerated and reused.



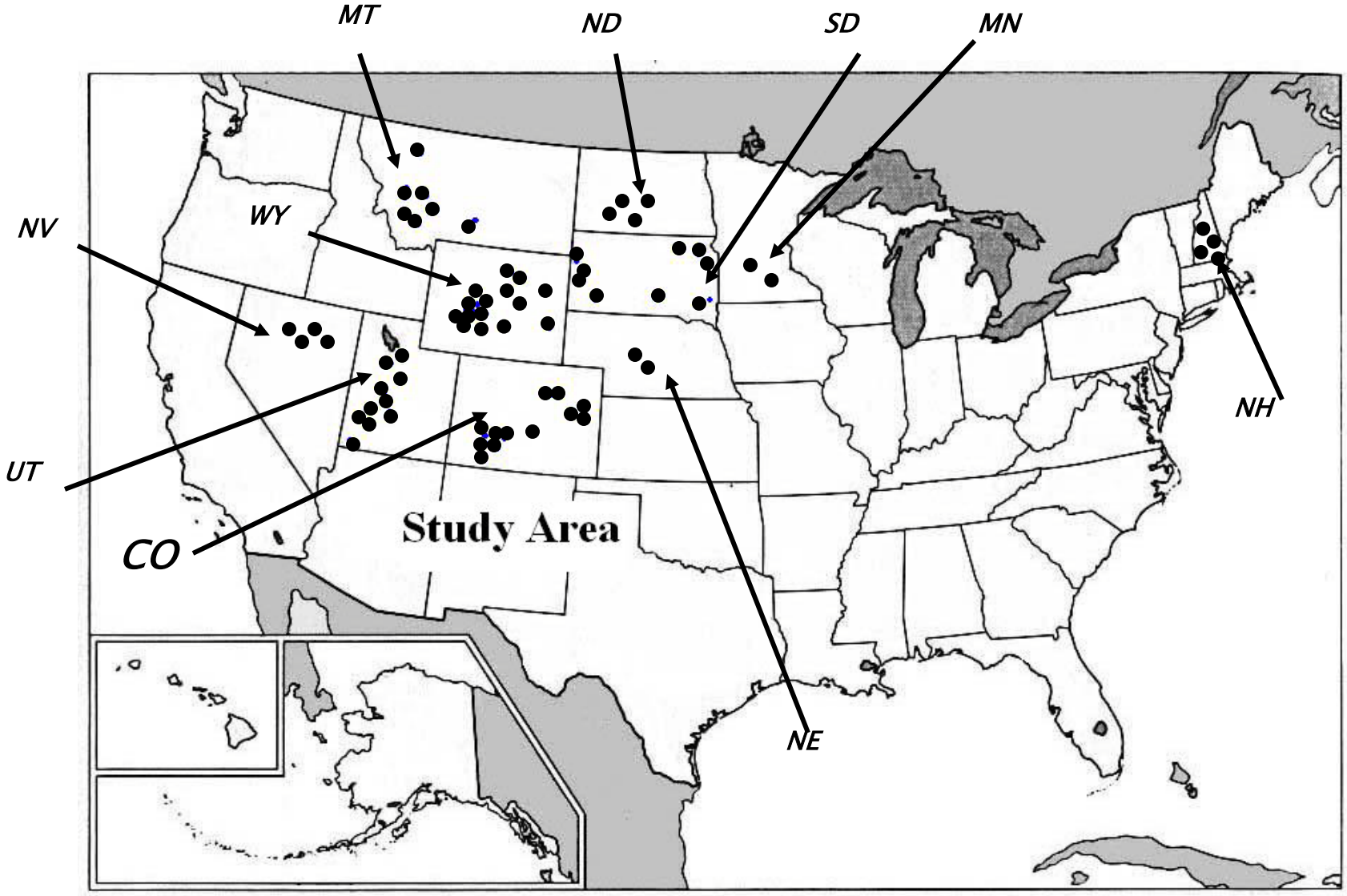
Surface area = 85 m2/g
Size = 12-18 nm



Present Studies

- Determine occurrence of arsenic in groundwaters of small communities in US.
- Study effectiveness of CuO particles in removal of arsenic in the presence of multiple competing ions under natural conditions.
- Determine CuO treatment effects on groundwater chemistry.
- We collected over 80 groundwater samples from small communities across US to study.

Groundwater Sampling for Arsenic Analysis



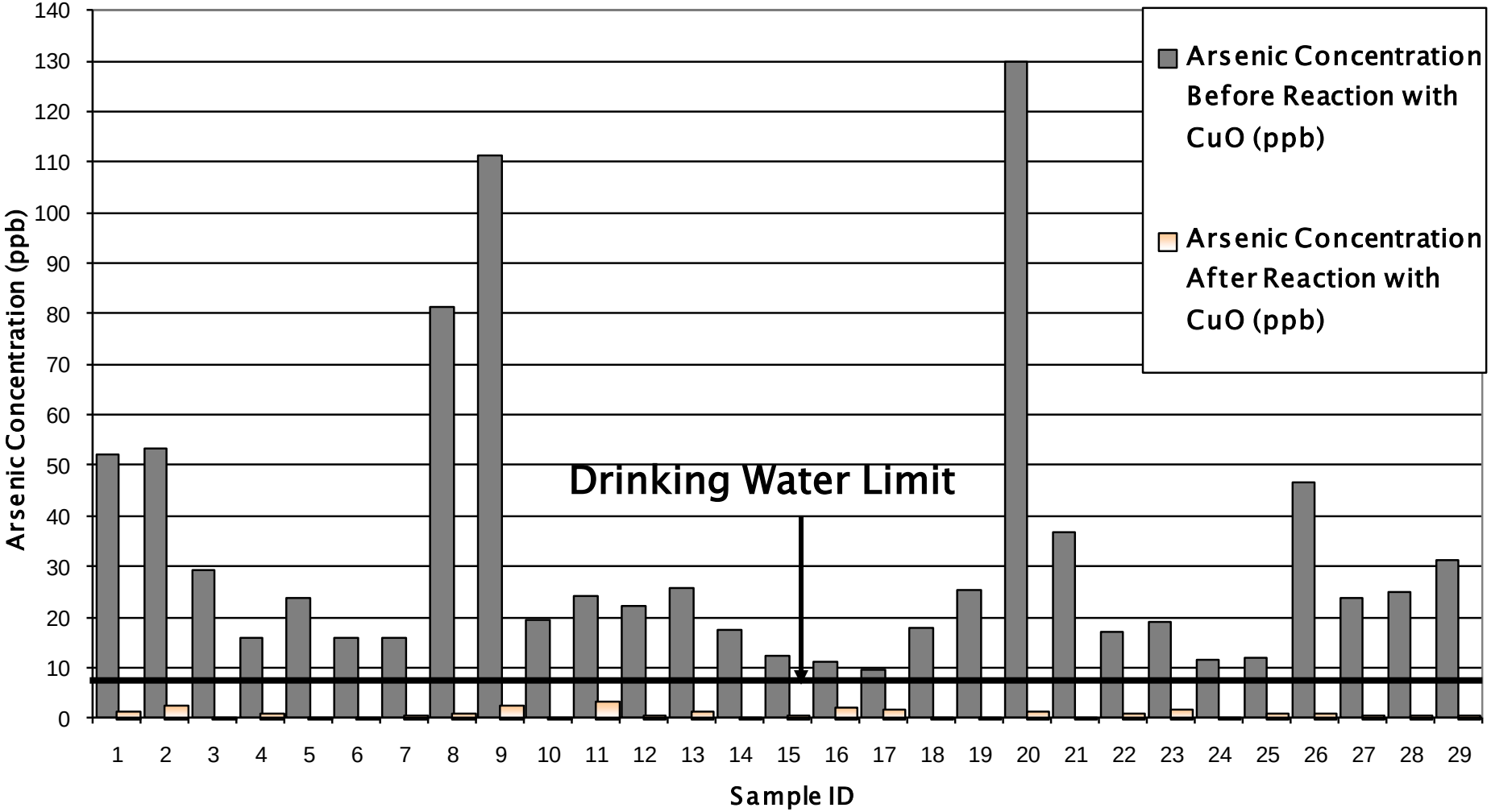
CuO Treatment Studies

- Groundwater samples were collected following WY-DEQ guidelines. Samples were collected in High Density Polyethylene (HFPE) bottles.
- The temp. pH, and ORP were measured on-site. Samples were filtered with 0.45 μm filters. A subsample was preserved with nitric acid.
- Acidified samples were analyzed for arsenic and major and trace elements with ICP-MS. Unacidified samples were analyzed for anions with IC.

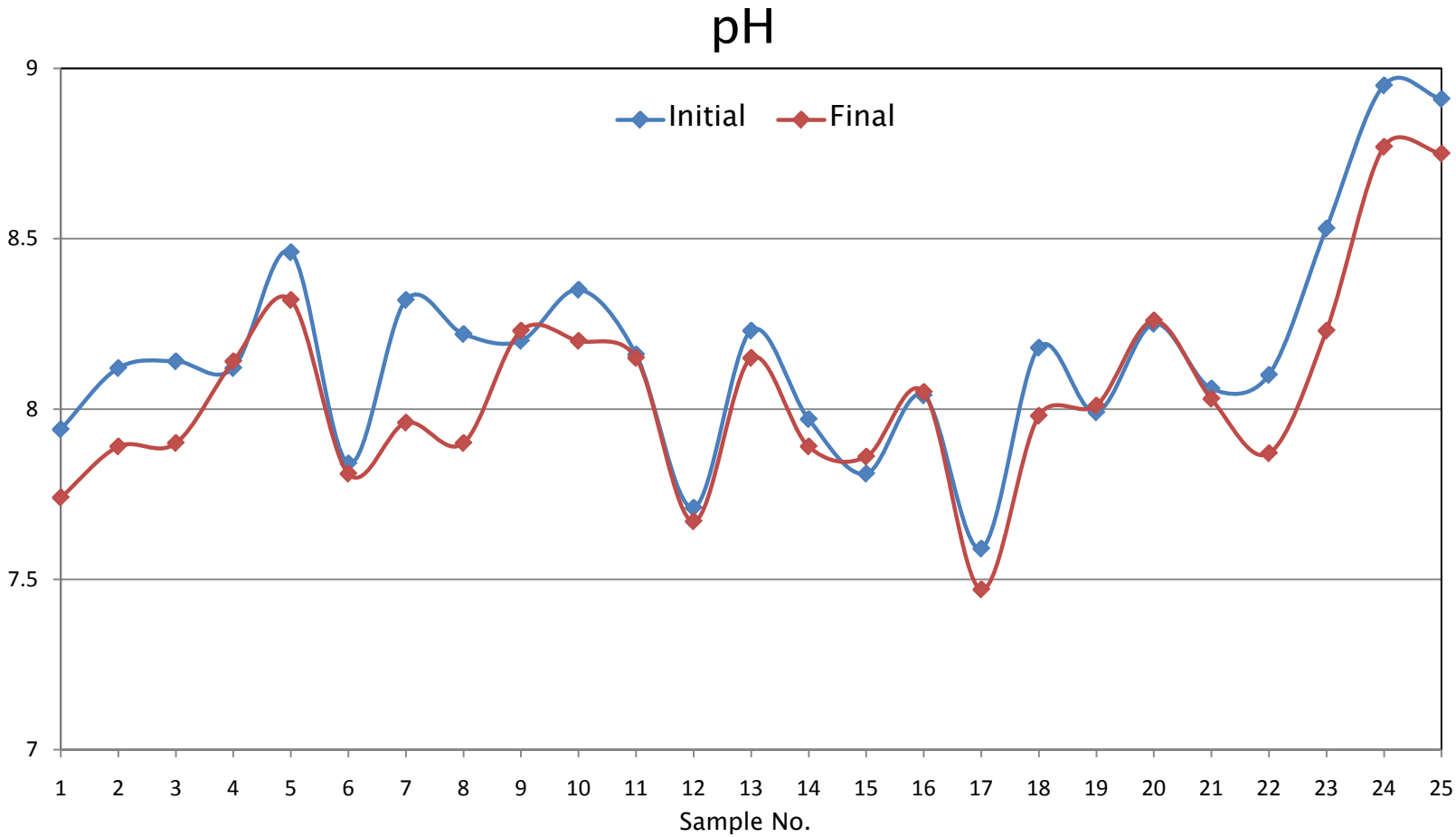
- Samples >10.0 μg/L As were reacted with 2g/L of CuO particles on a shaker for 30 minutes.
- After the reaction suspensions were filtered with 0.45 μm filters and clear filtrates were analyzed for arsenic, pH, and major and trace elements.

Out of 80 samples 55 exceeded the EPA HDWMCL for arsenic.

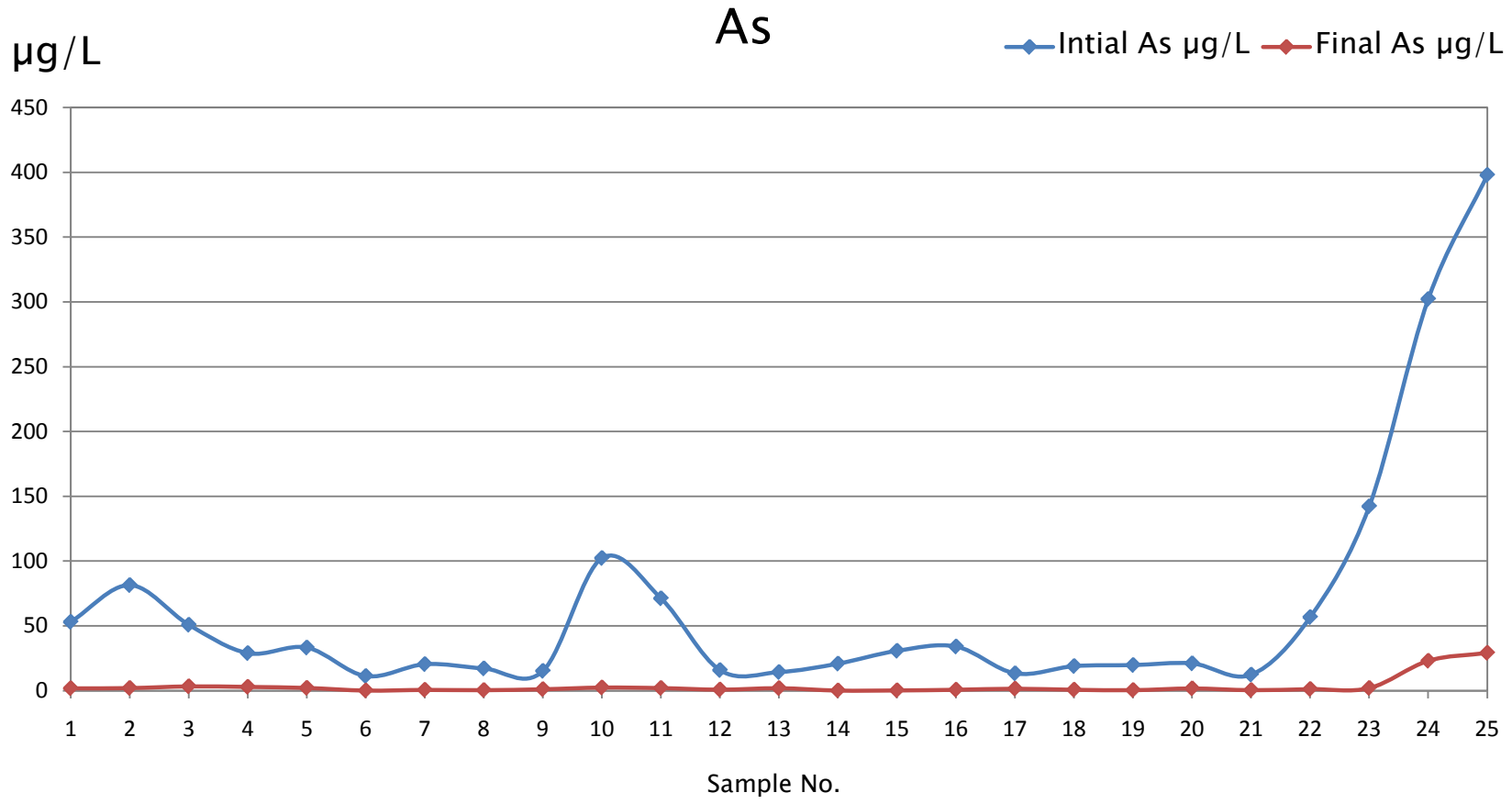
CuO Treatment Effect on Arsenic in Groundwater Samples



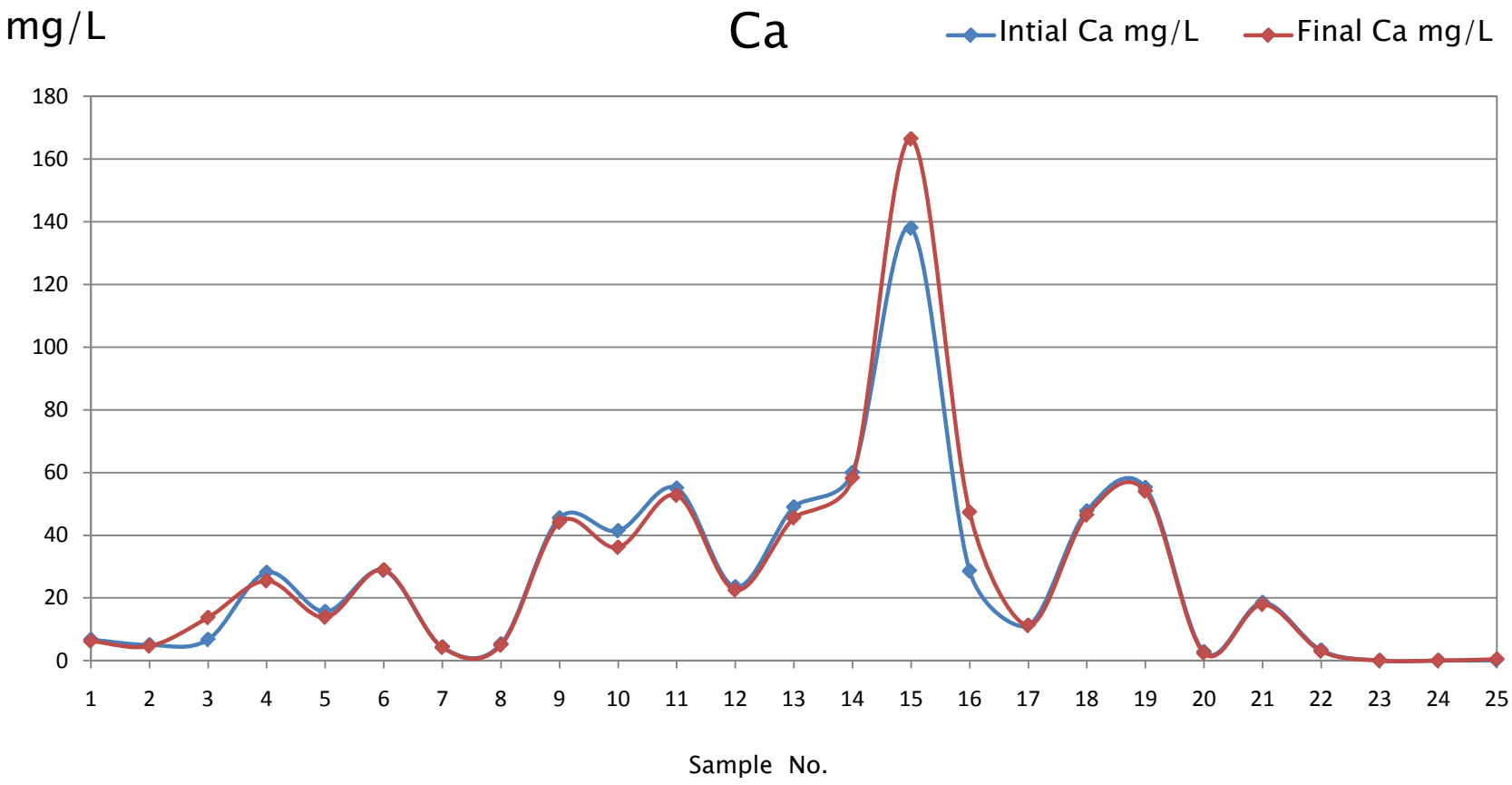
CuO Treatment Effect on pH



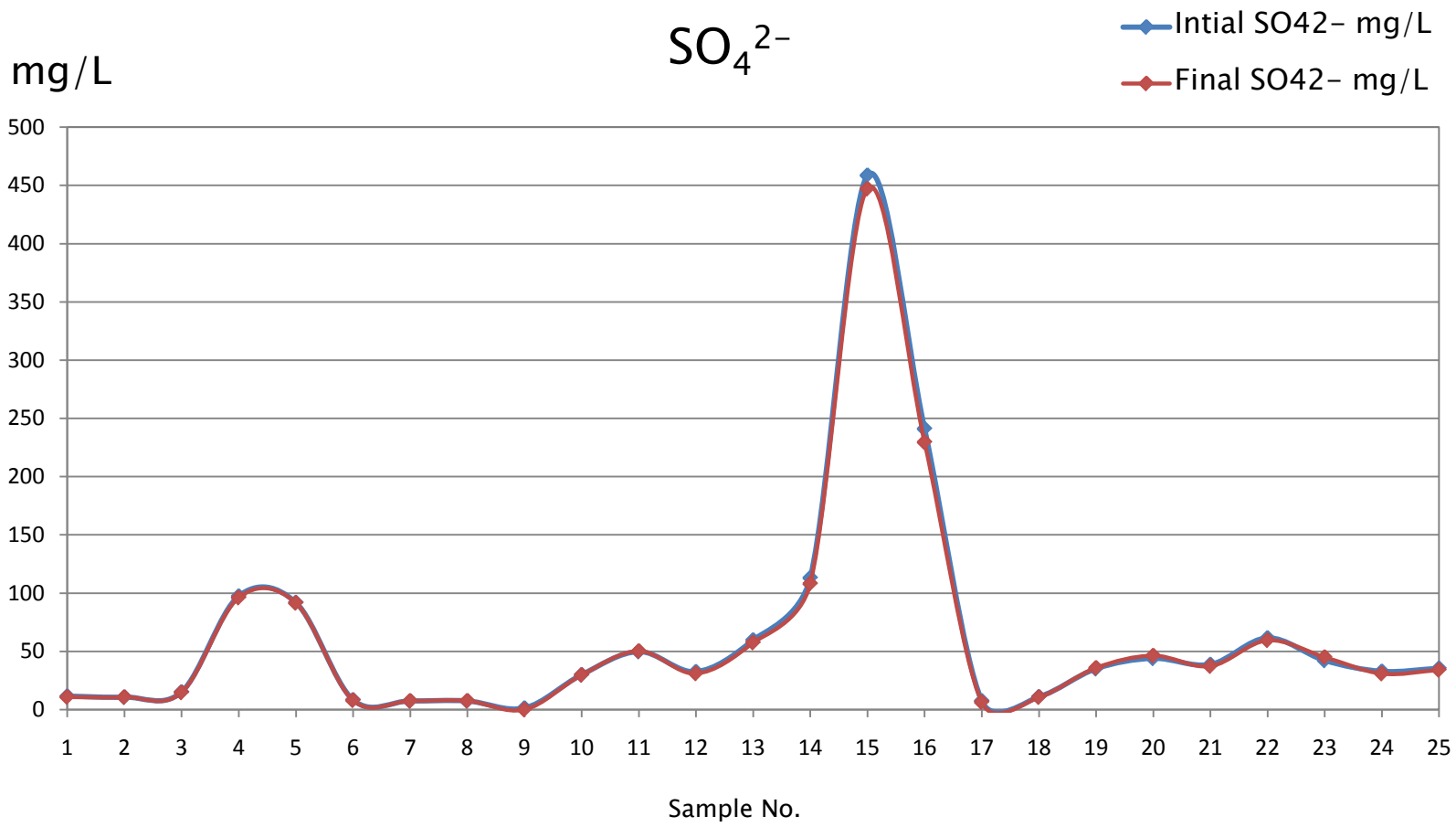
CuO Treatment Effect on Arsenic



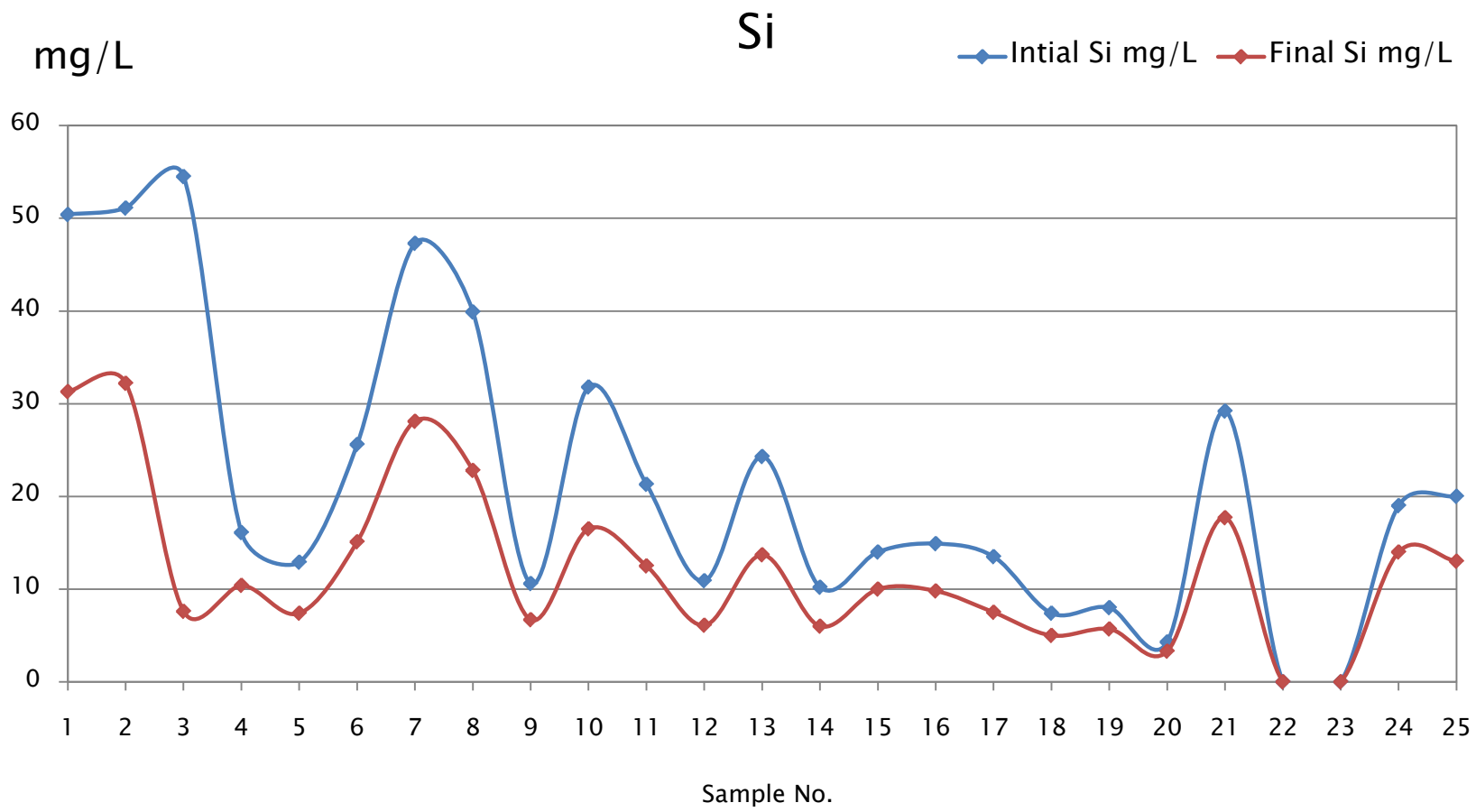
CuO Treatment Effect on Calcium



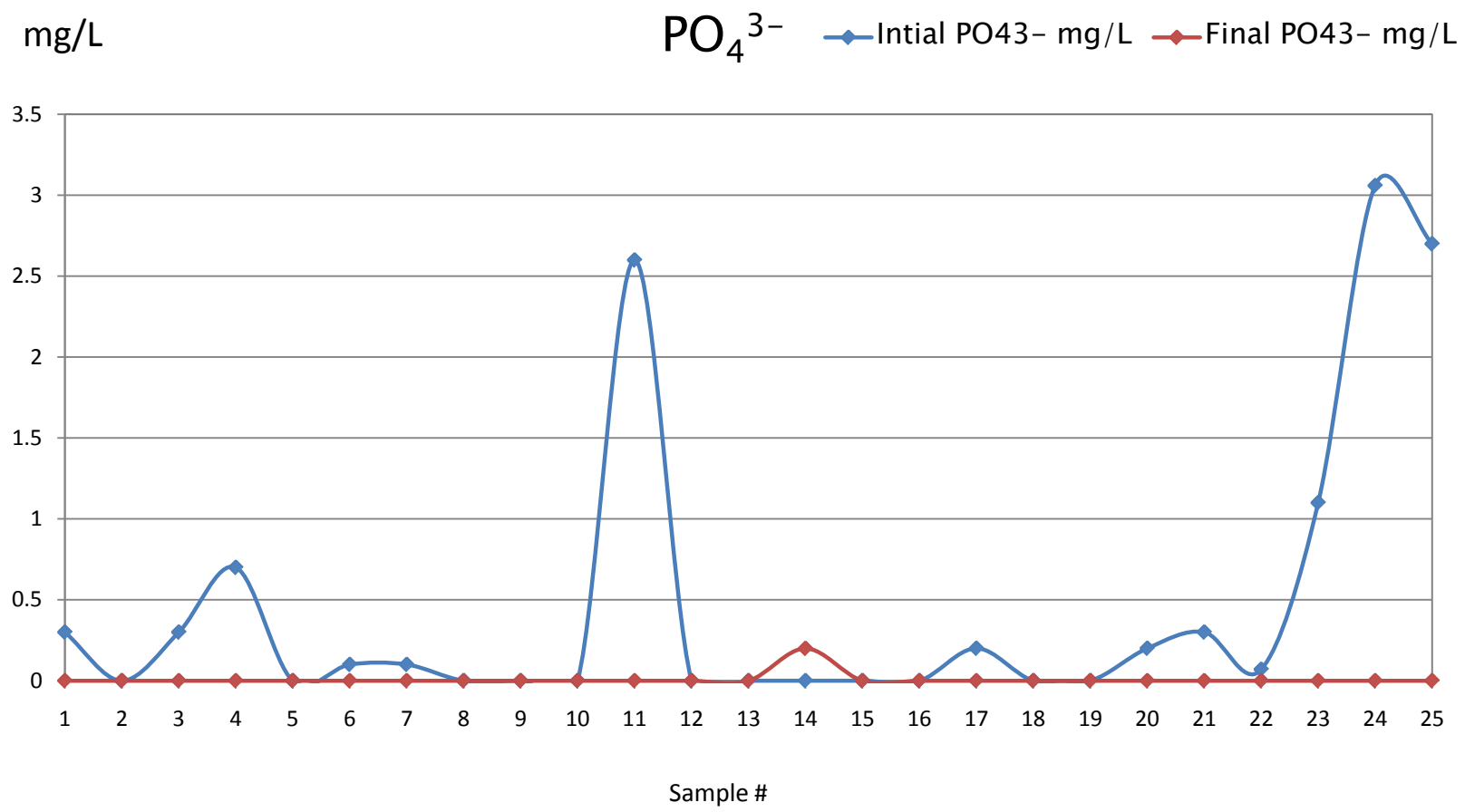
CuO Treatment Effect on Sulfate



CuO Treatment Effect on Silica



CuO Treatment Effect on Phosphate



CuO Treatment Effect on Trace Elements

#	Pb (µg/L)		Cr (µg/L)		Se (µg/L)	
	Before	After	Before	After	Before	After
1	<0.1	1.8	2.2	3	3.5	2.1
2	<0.1	1.4	1.4	3.2	4.3	1.6
3	<0.1	1.6	1.7	10	1.7	17.7
4	0.7	0.9	6.7	8.8	9.6	8.2
5	<0.1	0.3	7.5	9.4	16.1	15.2
6	0.6	0.3	6.2	4.8	1.4	1
7	0.5	0.3	3.7	4.6	0.9	0.7
8	0.2	0.2	4.1	5.2	0.4	0.3
9	<0.1	3.2	6.5	9.5	3.3	0.8
10	<0.1	4.6	6.9	9.5	3.3	1.7
11	<0.1	<0.1	7.2	10.8	3.3	1.7
12	<0.1	<0.1	1.6	2.9	1.1	<0.1
13	<0.1	0.2	2.3	7.9	3.5	5.6
14	<0.1	<0.1	<0.1	2.4	1.8	<0.1
15	<0.1	<0.1	8.3	9.8	1.7	<0.1
16	<0.1	<0.1	8.5	18	0.6	1
17	<0.1	<0.1	0.2	<0.1	1.4	2.8
18	<0.1	<0.1	0.8	2.2	1.3	1.8
19	0.6	0.6	4.1	8.7	1.2	0.4
20	0.7	0.5	7.8	10.8	0.8	0.2
21	0.3	0.3	6.2	8.1	2	2
22	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
23	<0.1	<0.1	<0.1	<0.1	7.2	2.5
24	2.4	0.4	<0.1	<0.1	<0.1	<0.1
25	1.8	0.2	<0.1	<0.1	<0.1	<0.1
EPA HDWMCL*	15		100		50	

CuO Treatment Effect on Trace Elements

#	Mn (µg/L)		Cu (mg/L)		Fe (mg/L)	
	Before	After	Before	After	Before	After
1	1.6	0.1	0.05	0.04	<0.1	<0.1
2	2.6	<0.1	0.02	0.04	<0.1	<0.1
3	3.9	<0.1	0.03	0.07	<0.1	<0.1
4	0.6	<0.1	0.05	0.05	<0.1	0.1
5	0.2	<0.1	0.02	0.06	<0.1	<0.1
6	0.4	0.1	0.01	0.03	0.1	0.1
7	0.1	0.2	0.01	0.01	<0.1	<0.1
8	4.1	0.2	0.01	0.01	<0.1	<0.1
9	1859	361	0.01	0.98	0.1	0.1
10	1	0.2	0.04	0.58	0.1	0.1
11	427	81.7	<0.01	0.04	0.1	0.1
12	4	0.1	0.05	0.03	<0.1	0.1
13	0.9	0.1	<0.01	0.08	0.1	0.1
14	3.6	0.1	0.02	0.03	0.1	0.2
15	7.3	45	<0.01	0.01	0.4	0.5
16	4.9	3.1	<0.01	0.22	0.1	0.1
17	0.3	<0.1	0.01	0.03	<0.1	<0.1
18	0.7	<0.1	<0.01	0.02	0.1	0.1
19	0.4	0.1	0.01	0.03	0.2	0.2
20	5.6	0.1	0.02	0.03	<0.1	<0.1
21	1.3	0.2	0.02	0.03	<0.1	<0.1
22	2.4	<0.1	0.01	0.03	<0.1	<0.1
23	23.6	3.5	0.04	0.08	0.2	<0.1
24	22	7	0.02	0.42	0.3	<0.1
25	33.1	5.5	0.03	0.25	0.2	<0.1
EPA HDWMCL*	50		1.3		0.3	

Simultaneous Competition of PO4, Si, and SO4 in Arsenic Removal

#	PO4	Si	SO4	%As Removed
1	0.3	50.4	11.5	96.6
2	BD	51.1	10.7	97.5
3	0.3	54.5	15.1	93.5
4	0.7	16.1	97.4	90
5	BD	12.9	91.9	93.7
6	0.1	25.6	8.4	99.1
7	0.1	47.3	7.4	97
8	BD	39.9	7.4	97.6
9	BD	10.6	1.3	92.8
10	BD	31.8	29.9	97.6
11	2.6	21.3	49.8	97.2
12	BD	10.9	32.5	94.9
13	BD	24.3	59.7	86.8
14	BD	10.2	113.1	99.5
15	BD	14	458.7	99.3
16	BD	14.9	241.1	97.9
17	0.2	13.5	7.5	88.8
18	BD	7.4	11	96.3
19	BD	8	35.1	97.9
20	0.2	4.3	44	91.9
21	0.3	29.2	38.7	96.7
22	0.07	<0.1	61.5	97.8
23	1.1	<0.1	42.2	98.5
24	3.06	19	32.8	92.4
25	2.7	20	35.41	92.7

Conclusions

- Out of 80 samples 55 exceeded the EPA HDWMCL for arsenic.
- CuO particles effectively removed arsenic across a wide-range of ground water chemistries, without pH adjustment or preoxidation step.
- Common ions in groundwater did not effect removal of arsenic with CuO particles.
- Currently, we are in the process of testing efficacy of CuO particles in removal chemical and biological contaminants of uranium produced water (PIs: Suzanne Clark, KJ Reddy, Sreejayan Nair, and Jodi Rene. Funding Source UW SER)

CuO and Arsenic Removal Studies

- Reddy, K.J., and Viswatej, A. 2005. A novel method to remove arsenate and arsenite from water. In: Proceedings of 8th International Conference on Biogeochemistry of Trace Elements*, Symposium on Arsenic in the Environment: Biology and Chemistry*, April 3-7, 2005, Adelaide, Australia.

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- Reddy, K.J., Viswatej, and T.R. Roth. 2007. Study of tenorite (CuO) particles in removal of arsenic under natural water conditions. In Zhu et al., (ed.) *Biogeochemistry of Trace Elements: Environmental Protection, Remediation, and Human Health,* Tsinghua University Press, Beijing, China.

- Carol M. Martinson and K.J. Reddy, 2009. Adsorption of As(III) and As(V) by CuO nanoparticles, *Journal of Colloid and Interface Science*, 336:406-411.

- Roth, T.R., and K.J. Reddy. 2009. Arsenic in the environment and its remediation by a novel filtration method. *Book Chapter (66).* In J. Bundschuh et al., (ed.) Natural Arsenic in Ground Waters of Latin America, Taylor and Francis Group, London, UK, pp605-614.

- Reddy, K.J. 2011. Method for removing arsenite and arsenate from water, U.S. Patent: 7,897,052

Acknowledgments

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