

Mercury Speciation, Bioavailability and Characterization of Contaminated Floodplain Soils

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Objectives of our project

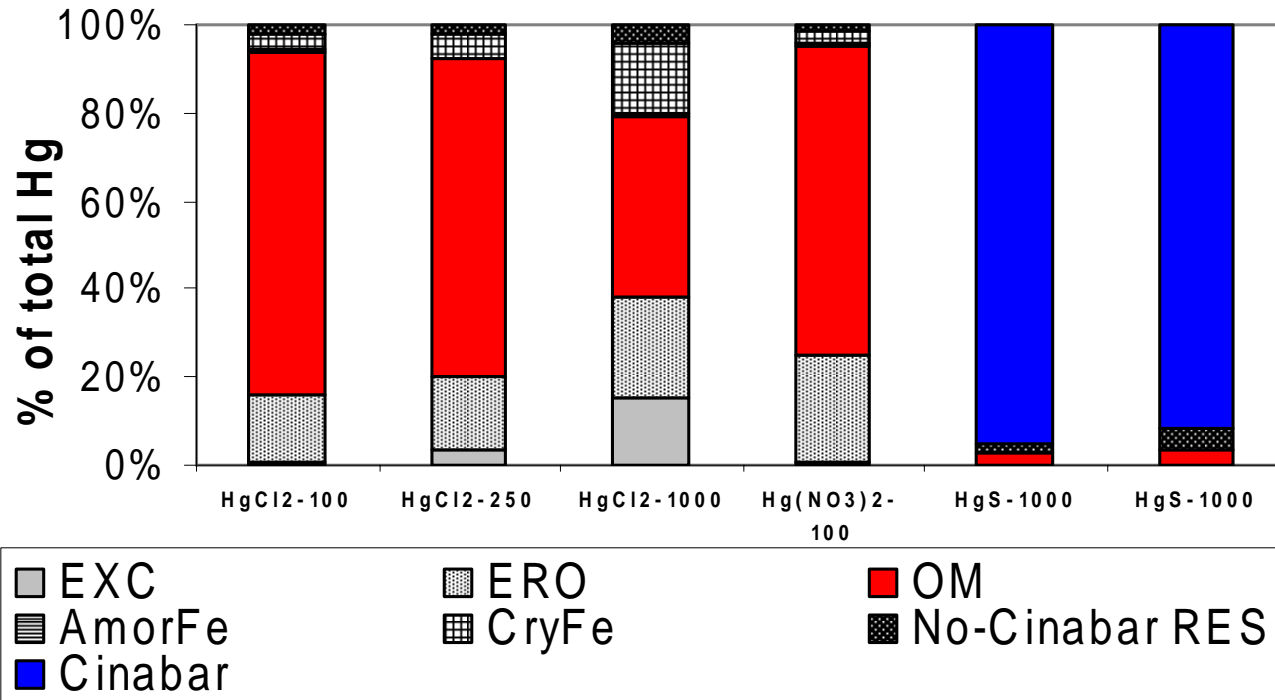
To investigate the mechanisms and major biogeochemical processes controlling mercury speciation, bioavailability, transformation and fate in contaminated soils, with special focuses on the **floodplain soils** of Oak Ridge ecosystem

Contents

- Mercury Speciation, Solid Phase Distribution, and Transformation
- Bioavailability of Mercury
 - Effects of Planting
 - Bioavailability of Mercury Fractions
 - Bioavailability of Mercury and HgS-Contaminated Floodplain soil
 - Extractability of HgS-Contaminated Floodplain soil
 - Other factors (Cl and oxides)
- Summary
- Future Plans

Mercury Speciation, Solid Phase Distribution, and Transformation

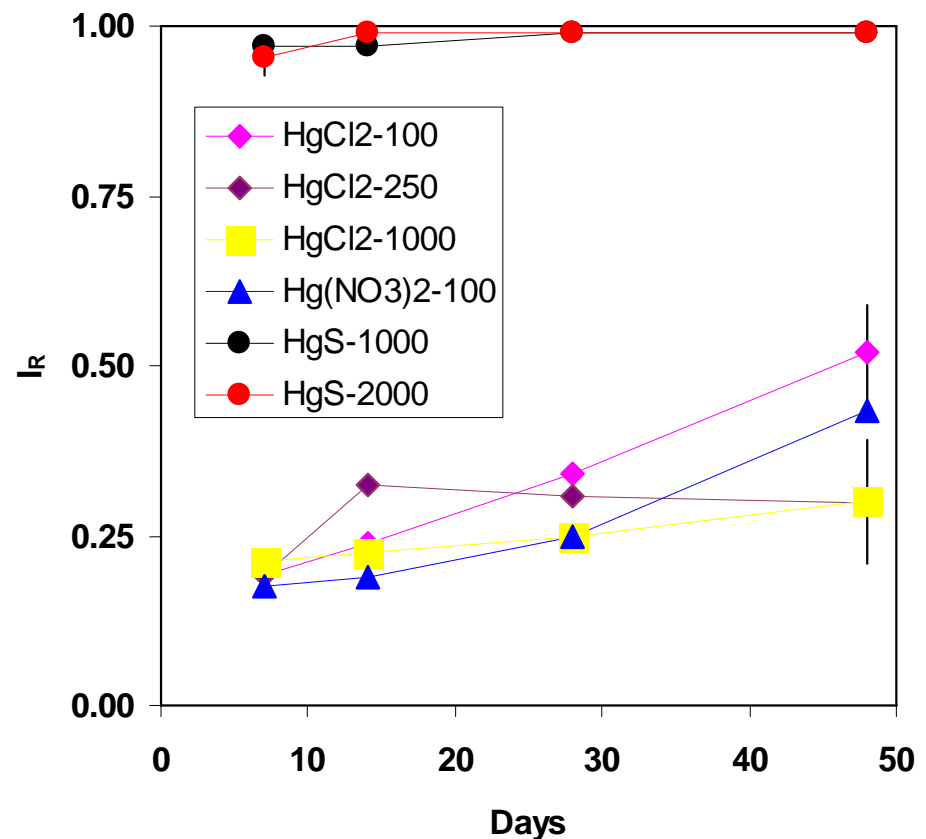
Mercury Speciation, Solid-phase Distribution



- Organically bound mercury species are the major solid-phase fraction in the floodplain soils contaminated with soluble mercury compounds
- Mercury is mainly present in the cinnabar fraction in HgS-contaminated soil.

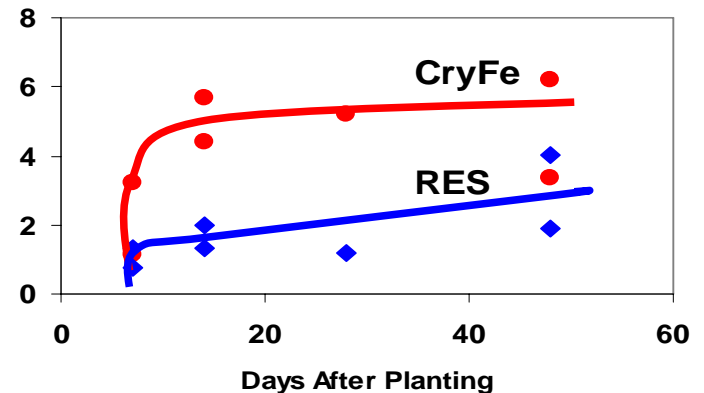
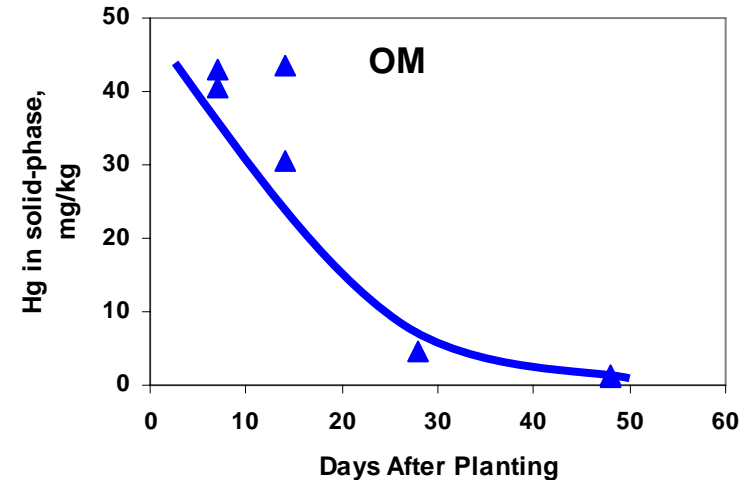
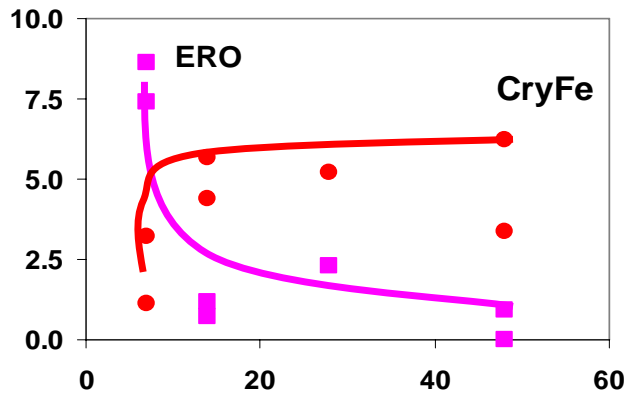
Redistribution and Transformation of mercury

- Redistribution and transformation of mercury from more labile fractions into more stable fractions were observed, resulting in increasing mercury binding intensity in soils.
- I_R is the relative binding intensity of mercury in soil/sediment.



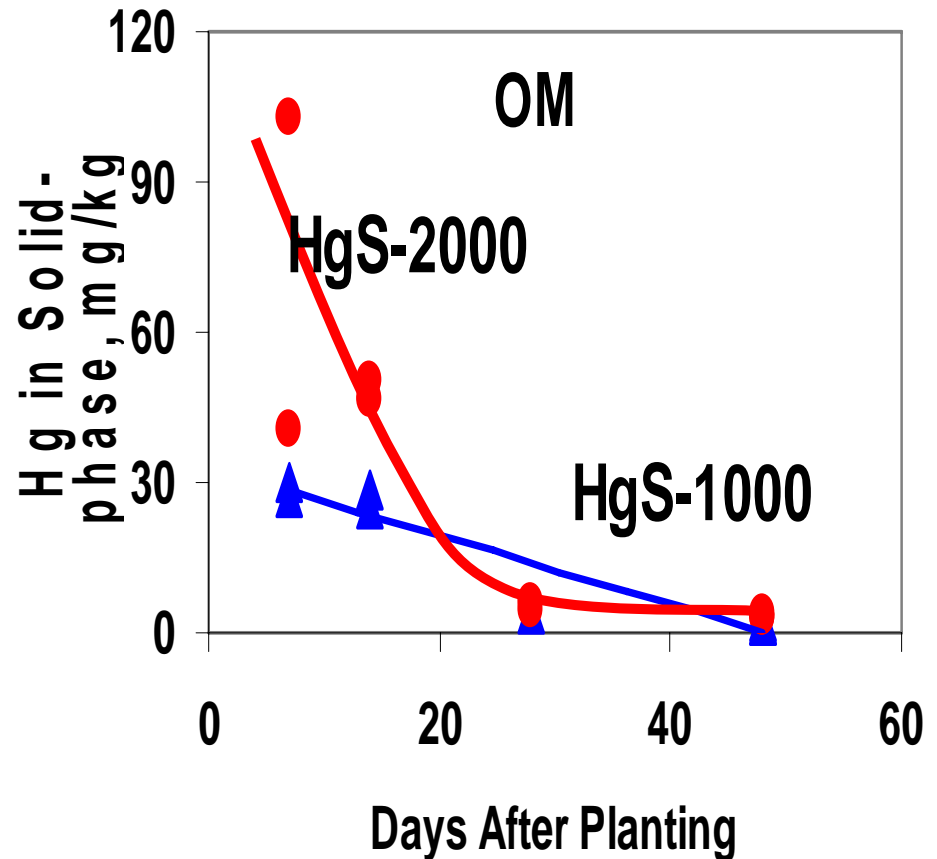
Mercury Transformation in Floodplain soils, HgCl₂-100

- Mercury in the Organic matter, easily oxide bound fractions was transferred into crystalline iron oxide bound and most stable residual fractions during a season of growing of plants.



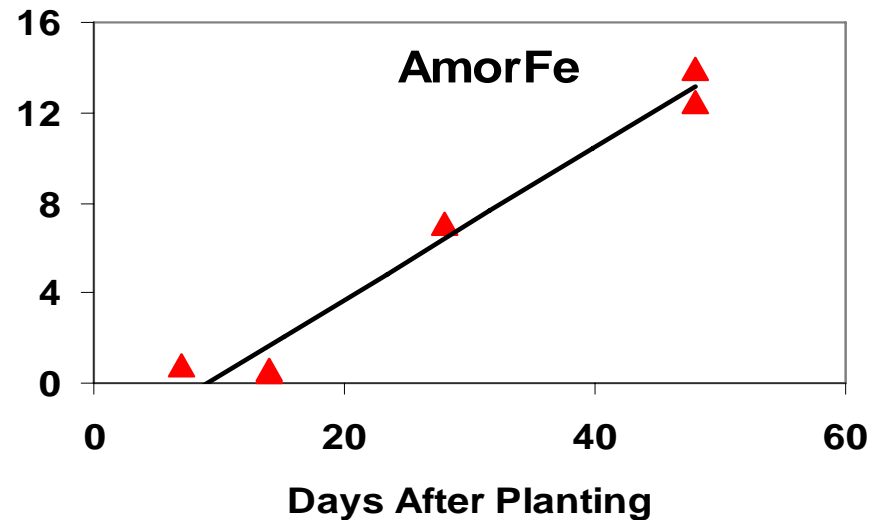
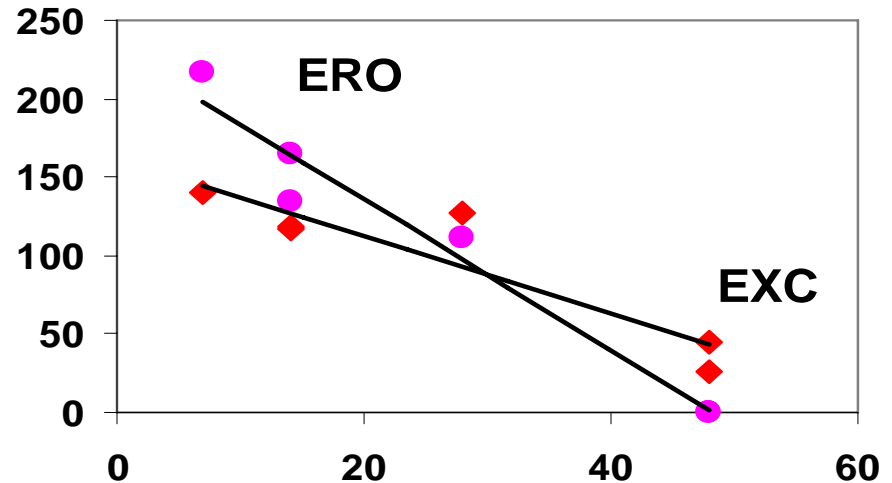
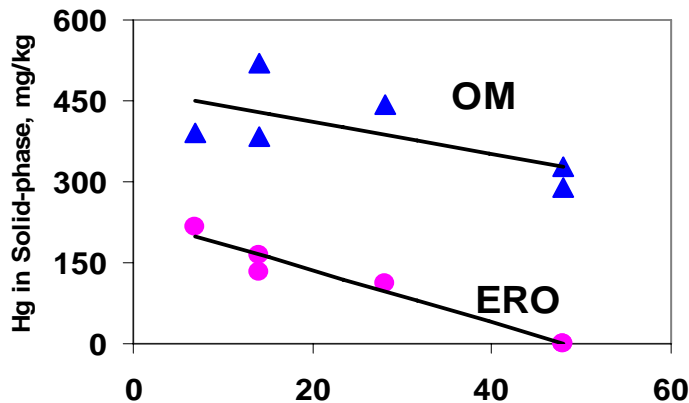
Mercury Transformation in Floodplain soils, HgS contaminated floodplain soil

- The organically bound fraction of mercury in mercury sulfide contaminated floodplain soil decreased over planting periods (Chinese brake fern) significantly.

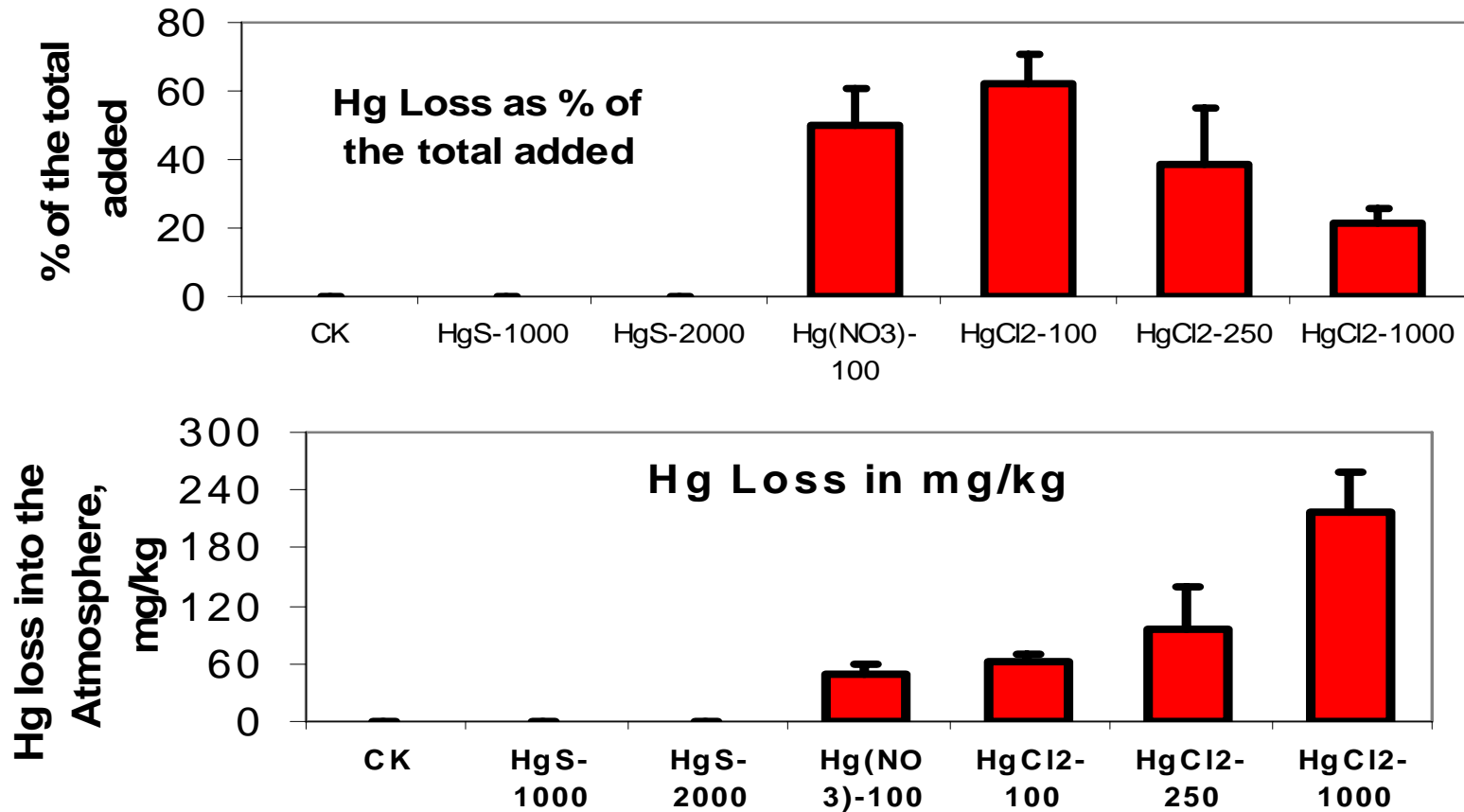


HgCl₂-1000

- In highly contaminated soils, mercury was quickly transferred from the exchangeable form, easily reductive oxide and organic bound fractions into amorphous iron oxide bound fraction as well as volatilization.



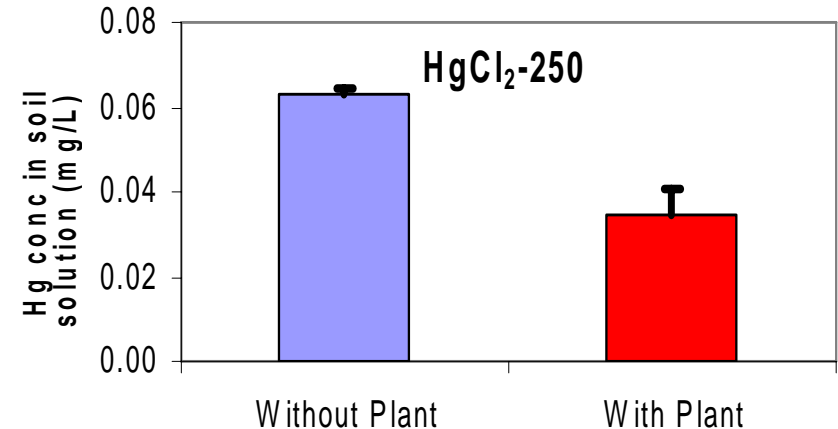
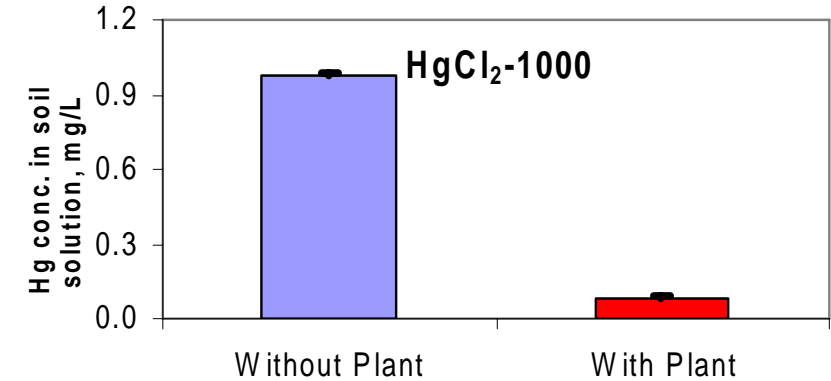
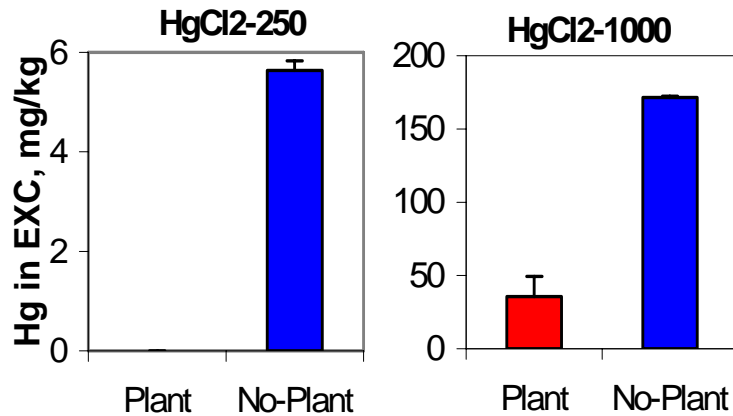
Net volatilization of mercury Floodplain soil with various mercury species



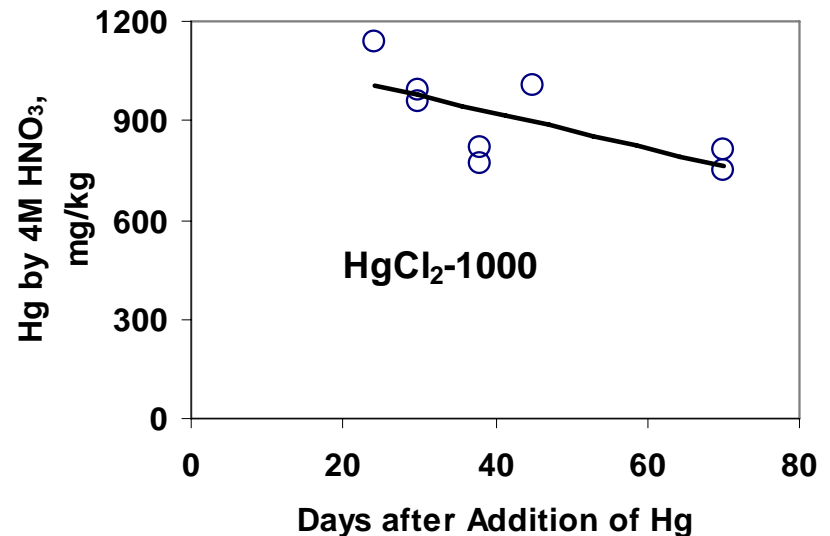
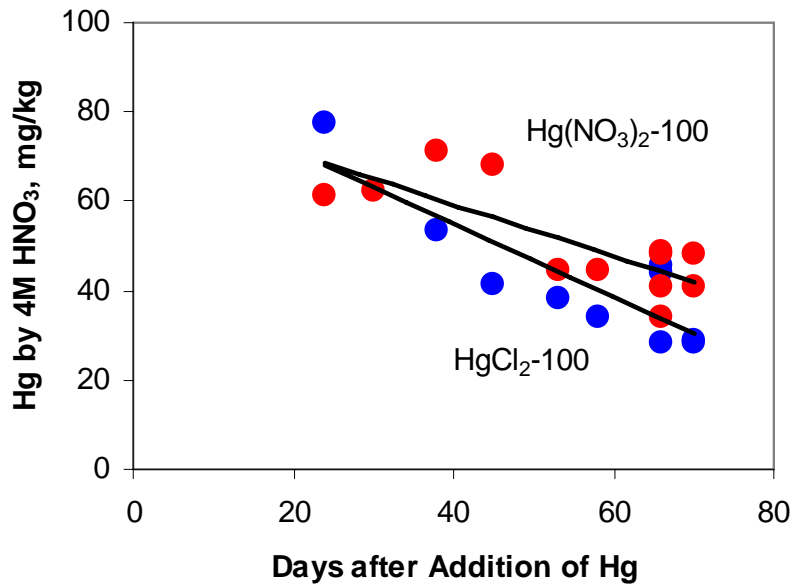
Mercury Bioavailability

Effects of Planting

- Planting (Chinese brake fern) for a growing season significantly decreased mercury concentrations in soil solutions and exchangeable forms, which are the most bioavailable form in soils

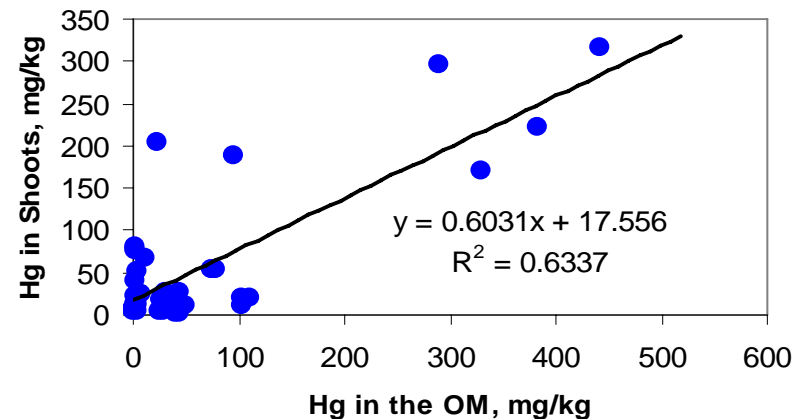
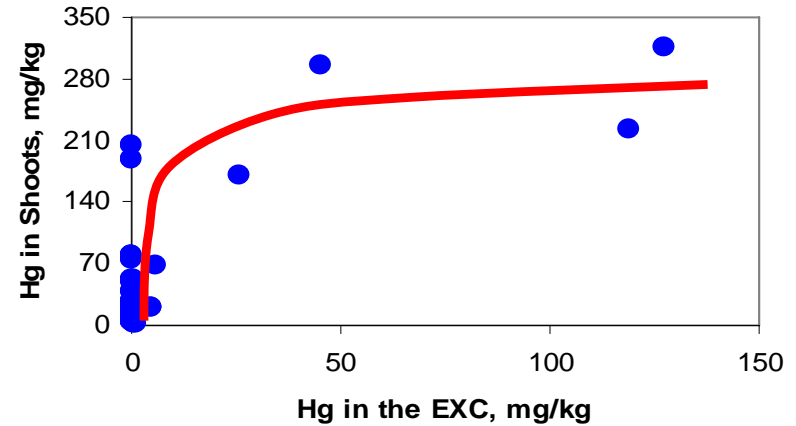


Planting (Chinese brake fern) for a growing season significantly reduced total mercury extracted by 4M HNO₃, which is the total non-cinnabar form mercury.



Bioavailability of Mercury Fractions

- Exchangeable mercury and organic bound mercury are most bioavailable mercury fractions among various solid-phase components



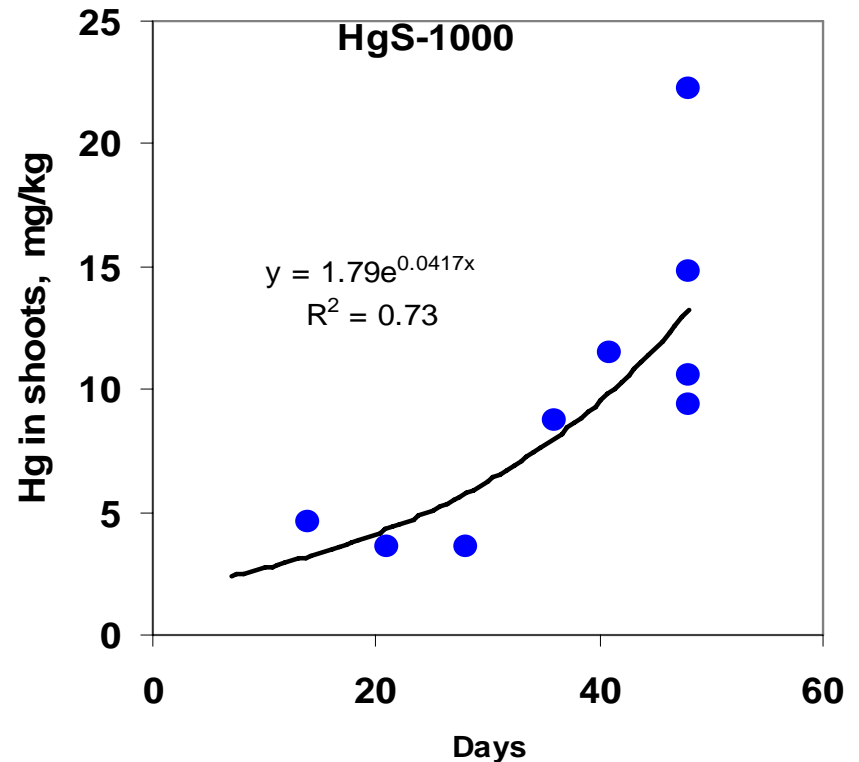
Bioavailability of HgS-contaminated floodplain soils

Plant (variety)	Year	Treatment HgS	mg/kg		
			Shoots	Roots	
Pteris vittata (48 Days growing)	Spring, 2004	CK	Avg	4.10	7.40
			Stdev	1.60	2.90
		1000	Avg	14.3	36.9
			Stdev	5.00	5.80
		2000	Avg	10.6	45.5
			Stdev	1.60	8.70
Pteris vittata (60 Days growing)	Spring, 2005	CK	Avg	0.8	BD
			Stdev	1.8	
		1000	Avg	13.3	132
			Stdev	14.4	75.6
		2000	Avg	24.2	297
			Stdev	24.7	229
Indian mustard (Long standing) (53 Days growing)	Spring, 2006	CK	Avg	0.20	2.22
			Stdev	0.32	0.50
		1000	Avg	26.8	84.0
			Stdev	25.2	39.4
		2000	Avg	15.2	205
			Stdev	23.2	45.5
Indian mustard (Florida broadleaf) (53 Days growing)	Spring, 2006	CK	Avg	0.95	2.41
			Stdev	1.07	0.53
		1000	Avg	34.7	17.1
			Stdev	29.2	11.1
		2000	Avg	78.8	87.0
			Stdev	50.8	42.7

BD: below detection limit of ICP-AES.

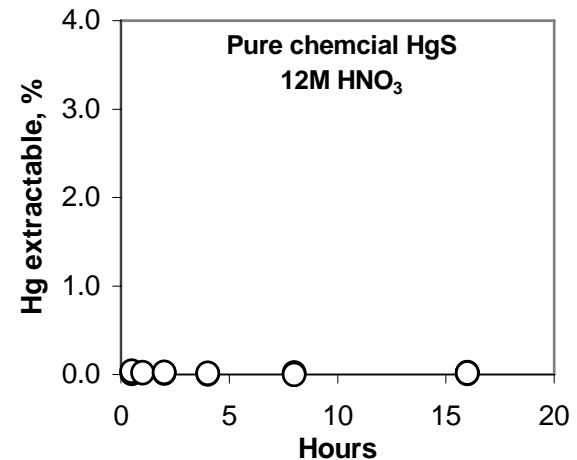
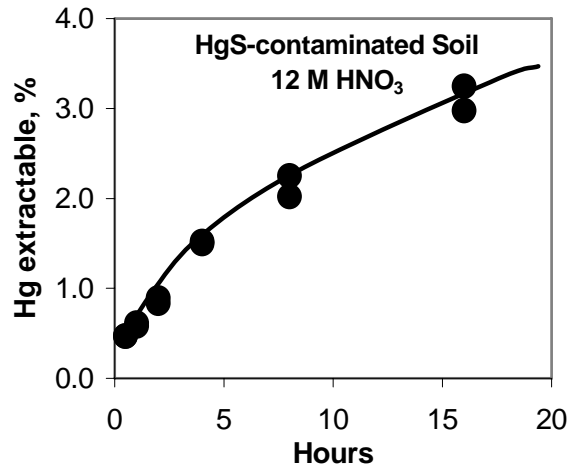
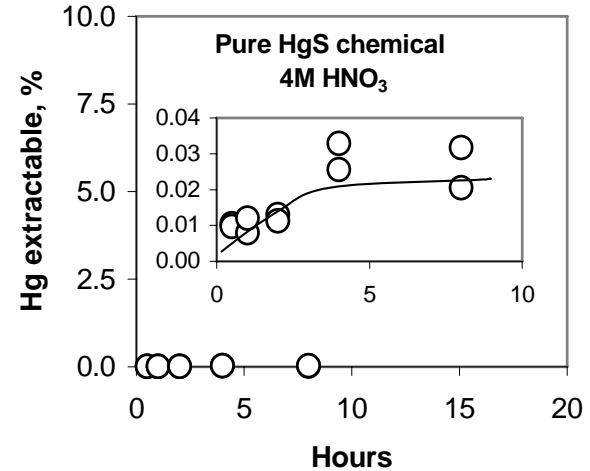
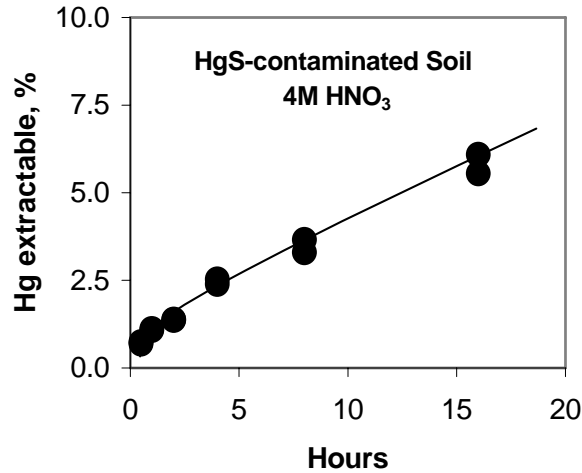
Bioavailability of HgS-contaminated floodplain soils, kinetics

- In HgS (cinnabar) contaminated floodplain soils, mercury still possesses to some extent bioavailability to plants (fern)



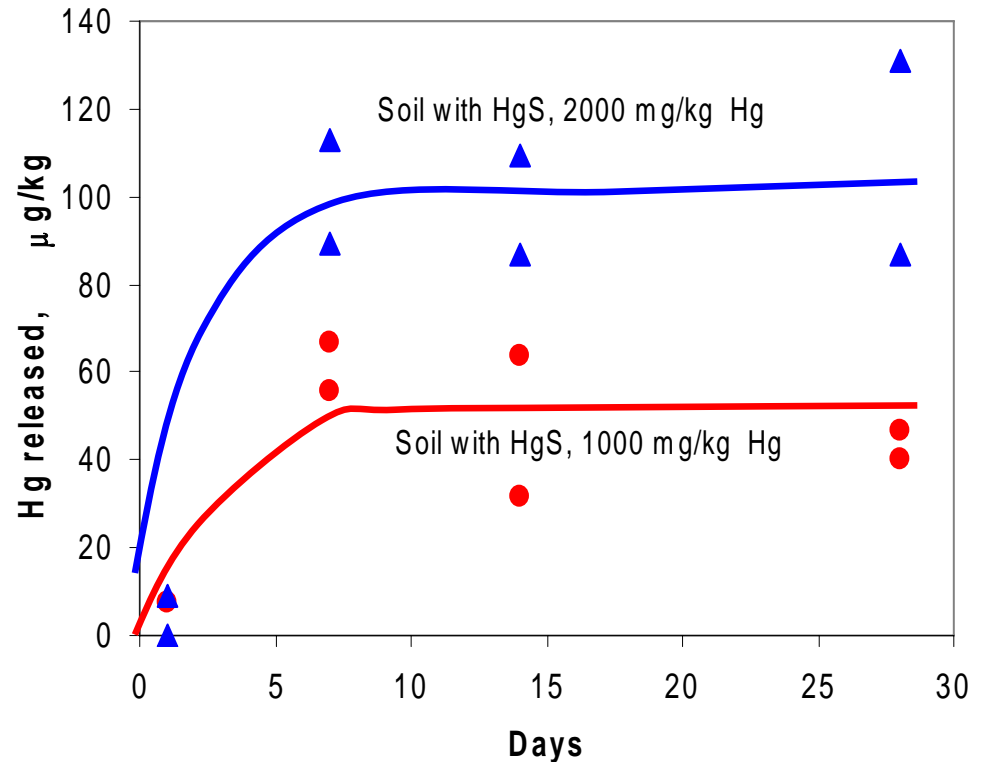
Extractability of HgS-contaminated floodplain soil, 4M/12M HNO₃.

Compared to pure HgS, Soil HgS has higher extractability



Extractability of HgS-contaminated floodplain soil, EDTA

- Mercury could be released from EDTA solution (0.05M EDTA)



Extractability of HgS contaminated floodplain soil by different chemical reagents.

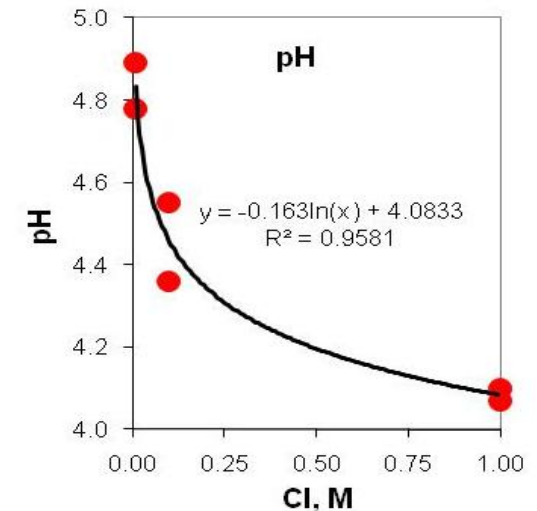
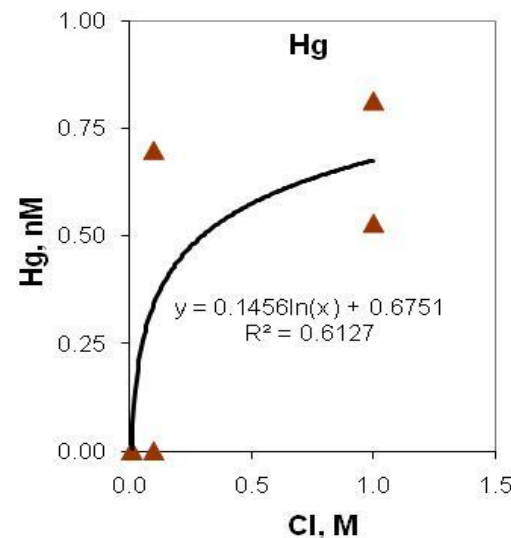
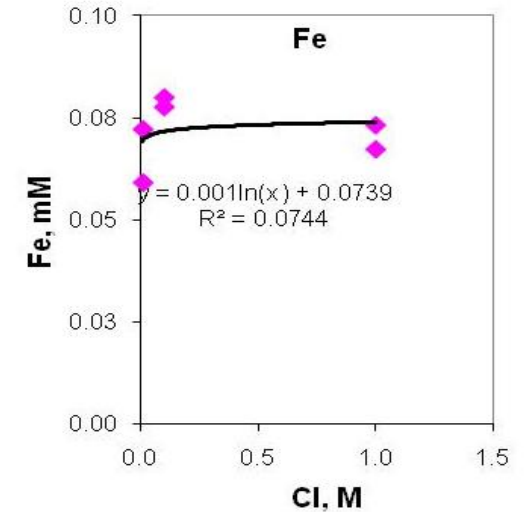
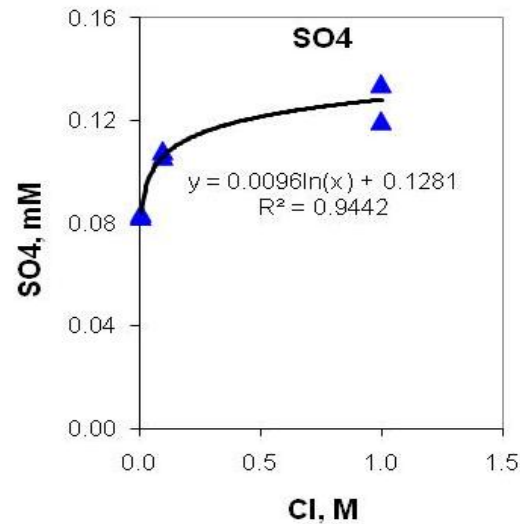
Reagents	Chemical HgS	HgS Contaminated Soils
Na ₂ S (saturated)	NM	99-100%
HCl:HNO ₃ :H ₂ O, (v/v/v, 1:6:7)	NM	98-100%
12 M HNO ₃	0.001-0.086%	0.47-3.25%
4 M HNO ₃	0.008-0.033%	0.69-6.08%
EDTA (0.05 M)	NM	0.01%
H ₂ O ₂	NM	0.13-5.13%
NH ₄ OAc	0	0
NH ₂ OH.HCl, pH 2	0	0

NM indicates not measured.

Effect of Cl⁻ on Reaction of HgS and Iron Oxides

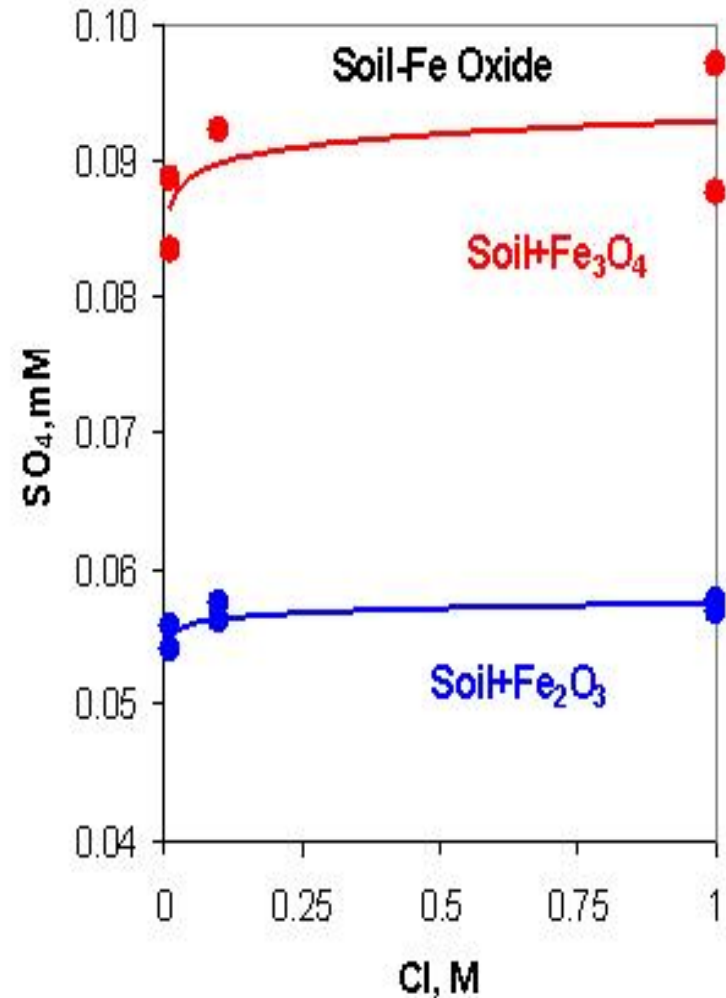
Addition of Cl to HgS and an iron oxide [Fe₃O₄ (magnetite) or Fe₂O₃ (hematite)] led to increased concentrations of Hg, Fe, and SO₄⁻².

In addition, a decrease in soil pH from 4.9 to 4.1 occurs.



Effect of Cl⁻ on Reaction of HgS and Iron Oxides

Addition of NaCl to contaminated Oak Ridge soil containing HgS, Fe₃O₄ (magnetite), and Fe₂O₃ (hematite) also led to increased concentrations of Hg, Fe, and SO₄⁻².



U.S. Provisional Patent Application

Cost-effective and highly efficient engineered nanophase material for the removal of arsenic (As), mercury (Hg), selenium (Se), chromium (Cr(VI)) from drinking water and other contaminated water) (DE-FC26-98FT-40395, U.S. Provisional Patent Application Series No: 60/556,494).

Summary

- Mercury is distributed among various solid-phase components. For soluble mercury contaminated floodplain soil, organic bound fractions was the major form, but for cinnabar-contaminated floodplain soil, HgS was the major form.
- Planting significantly changed mercury speciation in contaminated floodplain soil. Planting significantly reduced mercury in soil solution and exchangeable as well as 4M HNO₃ extractable mercury.
- Mercury was transferred from exchangeable and organic matter bound forms into other stable forms. Mercury volatilization occurred, especially in highly contaminated floodplain soils with soluble mercury.

Summary (cont.)

- Mercury in exchangeable and organic bound are most bioavailable. HgS in floodplain soils was to some extent bioavailable to plants and its extractability was higher than pure HgS chemicals by various extractants (4M/12M HNO₃, H₂O₂, EDTA).
- Increasing Cl⁻ concentration has been found to increase the chemical (and hence biological) availability of Hg in HgS-contaminated soils reacted with iron oxides.

Future Plans

- **Effects of Mn minerals** on bioavailability of contaminated floodplain soil.
- Simulated pilot experiments with field sediments and subsurface and surface soils from floodplain will be conducted to **assess the role of floodplain mercury as a source of downstream aqueous mercury**.
- Conduct the ecosystem assessment of **native plants for stabilization of floodplain** for better containing of mercury containment.
- Develop cost-effective and highly efficient natural and synthesized source nanomaterials for reactive barriers

Acknowledgements

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Recent Publications

- Han, F.X., W.D. Patterson, Y. Xia, B.B.M. Sridhar, and Y. Su. 2006. Rapid determination of mercury in plant and soil samples using inductively coupled plasma atomic emission spectroscopy, a comparative study. ***Water, Air and Soil Pollution*** 170: 161-171.
- Han, F.X., Y. Su, D.L. Monts, C.A. Waggoner, and M. J. Plodinec. 2006. Binding, distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA. ***Science of Total Environment*** 368: 753-768.
- Han, F.X. S.Shiyab, J. Chen, Y. Su, D. L. Monts, C. A. Waggoner. 2009. Extractability and Bioavailability of Mercury Sulfide Contaminated Soil from Oak Ridge, Tennessee, USA. ***Water, Air and Soil Pollution***.
- Su, Y., F.X. Han, J. Chen, Y. Xia, D.L. Monts. 2009. Bioavailability of mercury in contaminated oak ridge watershed and potential remediation of river/runoff/storm water by an aquatic plant. **Proceedings of the 12th International Conference on Environmental Remediation and Radioactive Waste Management**. ICEM09 October 11-15, 2009, Liverpool, UK.

Recent Publications (cont.)

- Han, F.X., S. Shiyab, Y. Su, D.L. Monts, C.A., Waggoner, and F. B. Matta. 2007. Bioavailability and stability of mercury sulfide in oak ridge (USA) Soils. **Proceedings of the 11th International Conference on Environmental Remediation and Radioactive Waste Management ICEM2007**, September 2-6, 2007, Oud Sint-Jan Hospital Conference Center, Bruges, Belgium.
- Han, F.X., S. Shiyab, Y. Su, D.L. Monts, C.A., Waggoner, F. B. Matta. 2007. Stability and bioavailability of mercury sulfide in oak ridge soils. **Proceedings of Waste Management (WM'07) Conference**, February 25-March 1, 2007, Tucson, AZ.
- Monts D.L., **F.X. Han**, Y. Su, C.A. Waggoner, and M.J. Plodinec. 2005. Bioavailability and speciation of mercury in soils from Oak Ridge, Tennessee, USA. **Proceedings of The 10th International Conference on Environmental Remediation and Radioactive Waste Management**, September 4-8, 2005, Scottish Exhibition & Conference Centre, Glasgow, Scotland.
- Su, Y., **F.X. Han**, Monts D.L., C.A. Waggoner, and M.J. Plodinec. 2005. Bioavailability and speciation of mercury in soils from Oak Ridge, IN. **Proceedings of The 5th Annual Symposium on Waste Management, WM'05 Symposium**, February 27-March 3, 2005, Tucson, AZ