"Mercury Methylation of Aquatic Plants: Using XAS for speciation

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Water Hyacinth (*Eichhornia crassipes)*


Water hyacinth
Eichhornia crassipes
Photo by Ann Murray

- Non-native floating plant currently present in Delta region
- Clogs waterways
- Currently controlled with herbicides
- Fast growth rate
- Hyperaccumulator of heavy metals

Control of Water Hyacinth

- Methods of controlling hyacinth may be methods of mercury cleanup
  1) Chemical
  2) Biological
  3) Mechanical
     Shredding, Harvesting
- Methods may also affect Hg speciation

The Terminator at Dow Wetlands

Overall Approach

- Field Assessment
  - Collection of plant samples
  - Assessment for Total Hg using CVAAS

  Dow Wetlands, Pittsburg Ca

  Marsh Creek, Antioch CA
- Uptake Studies (Environmental Growth chamber)
  - Uptake rates
  - Methylation
  - Affect of shredding
- Speciation
  - XAS
- Concurrent Shredding studies:
  - Dow Wetlands, Lambert Slough

Hg Field Study Results: Dow Wetlands

Water (WQO=0.025 ppb)	0.577 ppb ± 0.138
Sediment (ERL= 150 ppb, ERM= 700 ppb)	273 ppb ± 71
Water Hyacinth	Roots 1.3 ppm Shoots 1.2 ppm

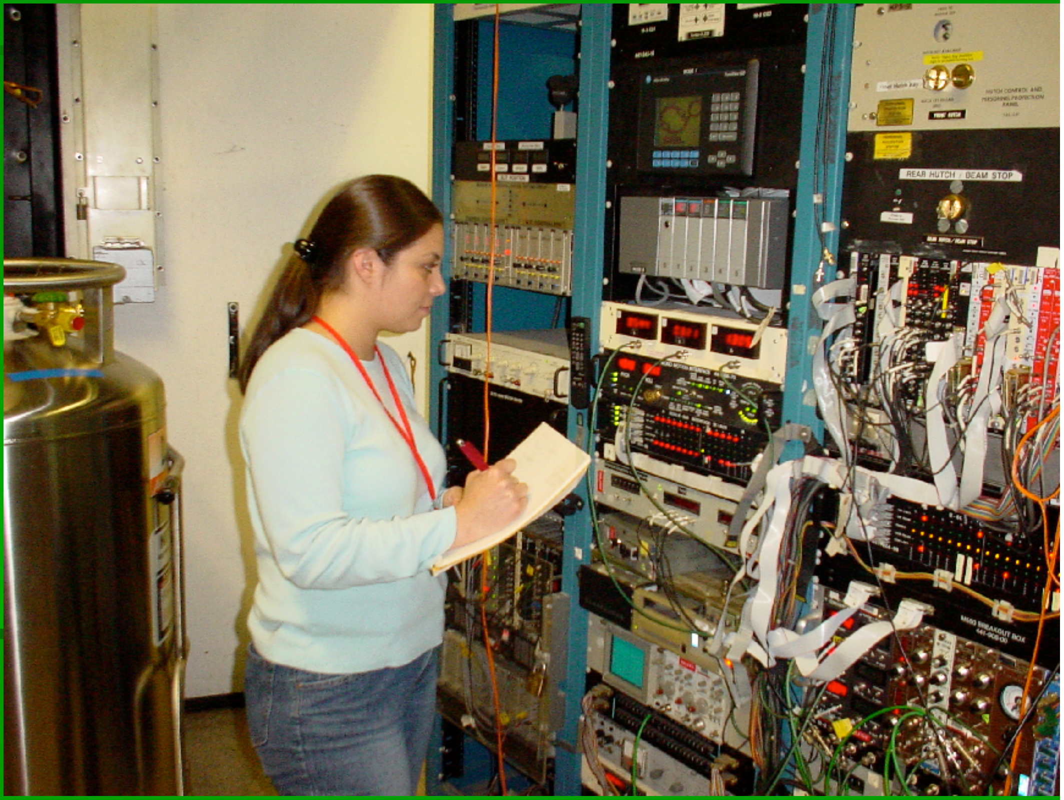
- Plants gathered in November 2003 after shredding
- Analysis with CVAA, $SnCl_2$ reduction, with EPA methods, quality control
- Values were calculated by averaging 10 samples

Hg Uptake study

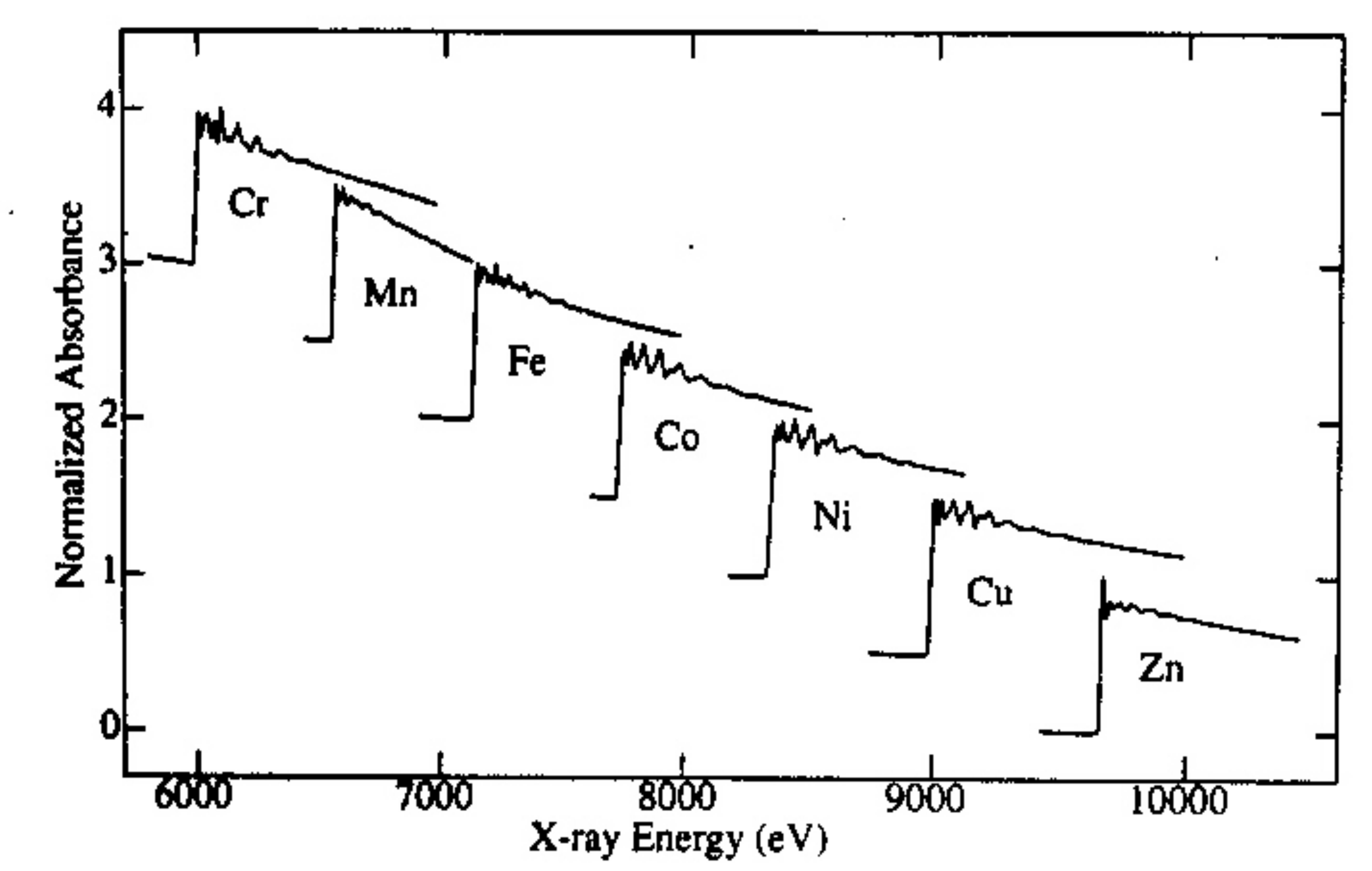
- **Lab chamber Study:** Plant samples were collected from the Dow Wetlands and grown in 1ppm $HgCl_2$ under
  - (1) aerobic conditions
  - (2) anaerobic conditions
  - (3) shredded plant material only (anaerobic)
- Total mercury: CVAA.
- Hg speciation: (XAS)

Preparation of Hyacinth for XAS

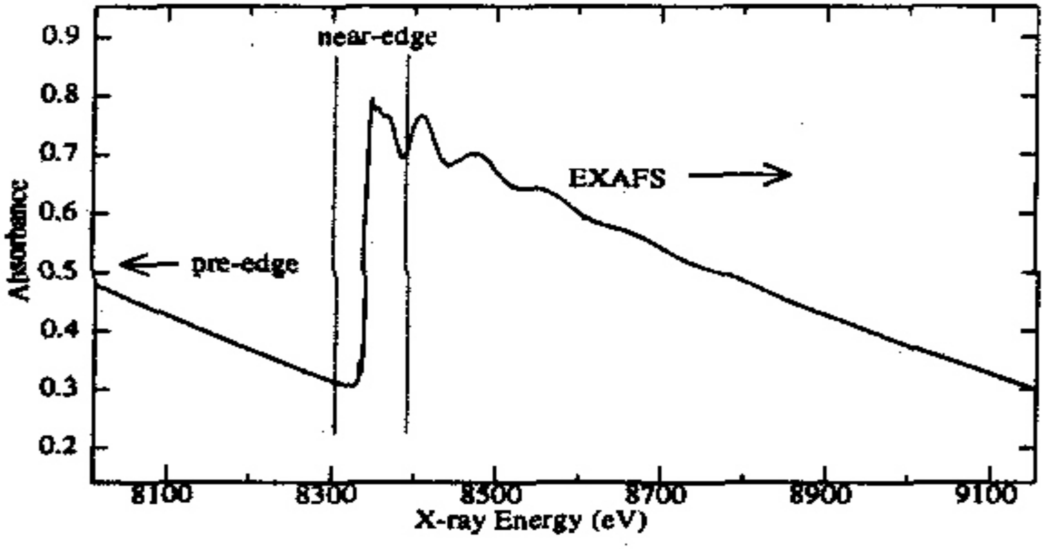
- Rinse, separate roots and shoots
- Freeze in liquid N_2, grind
- Mount in Aluminum spacers with mylar windows
- Model compounds all aqueous

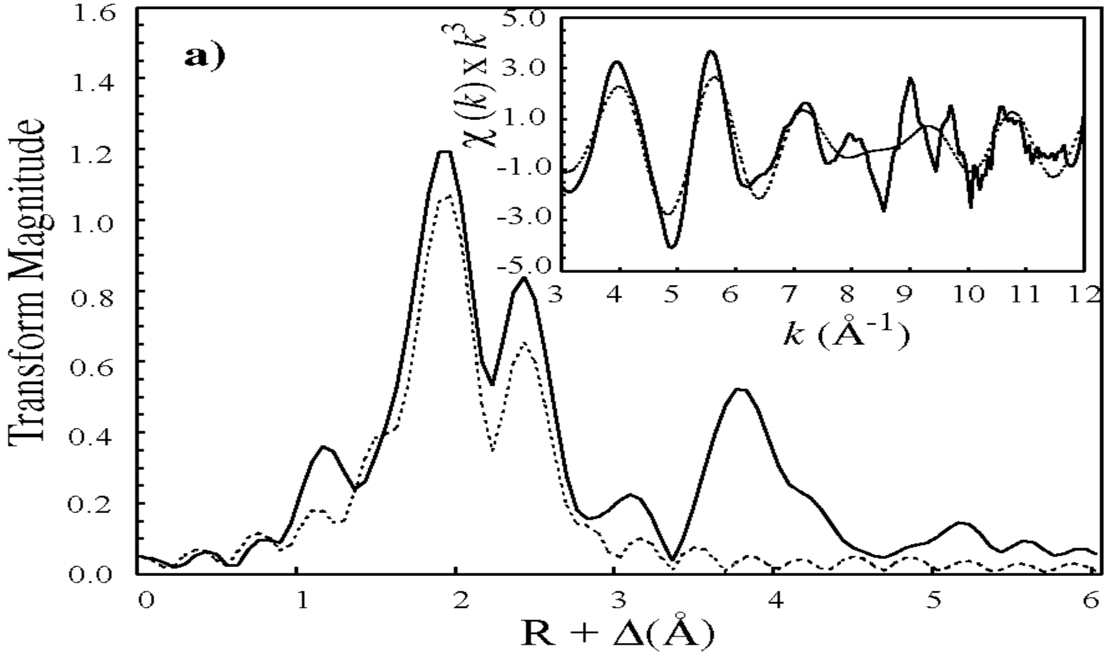


XAS of Various Elements



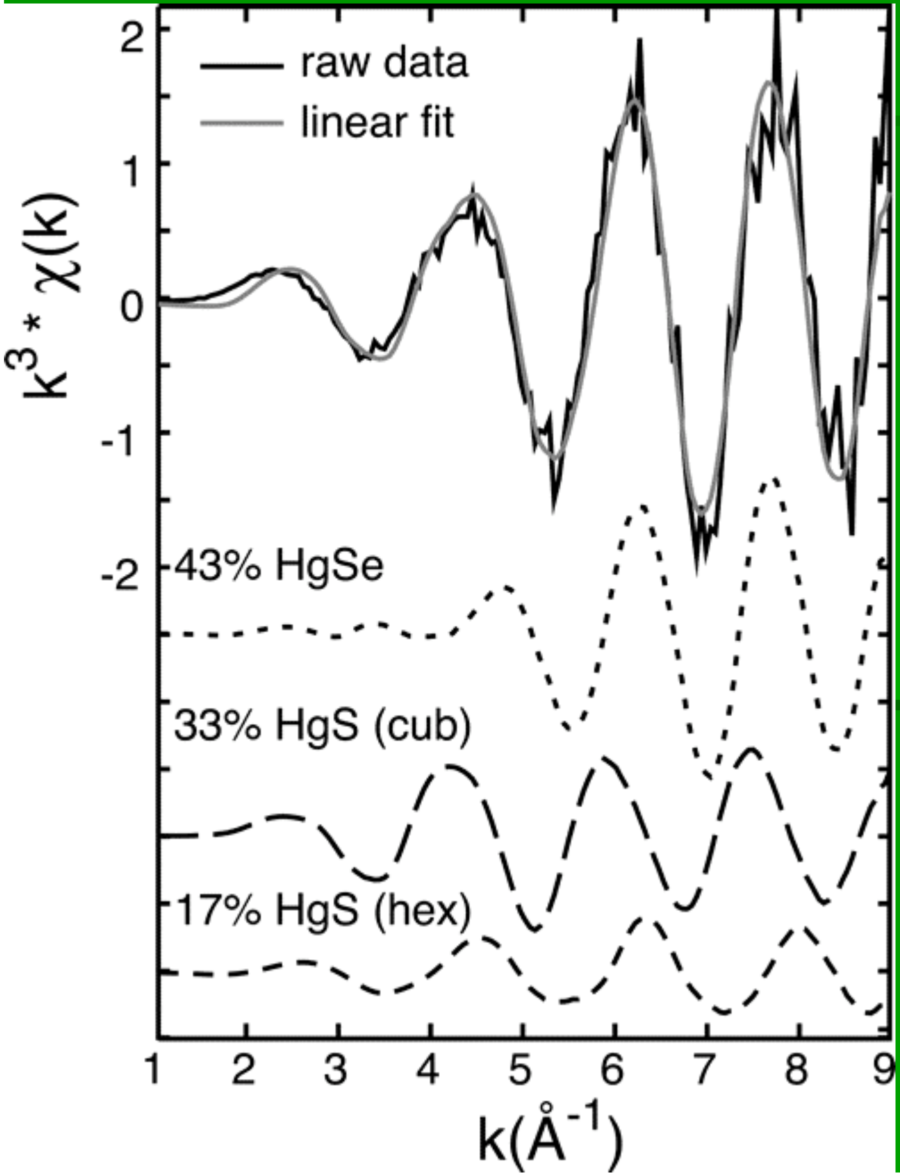
XAS: Concepts





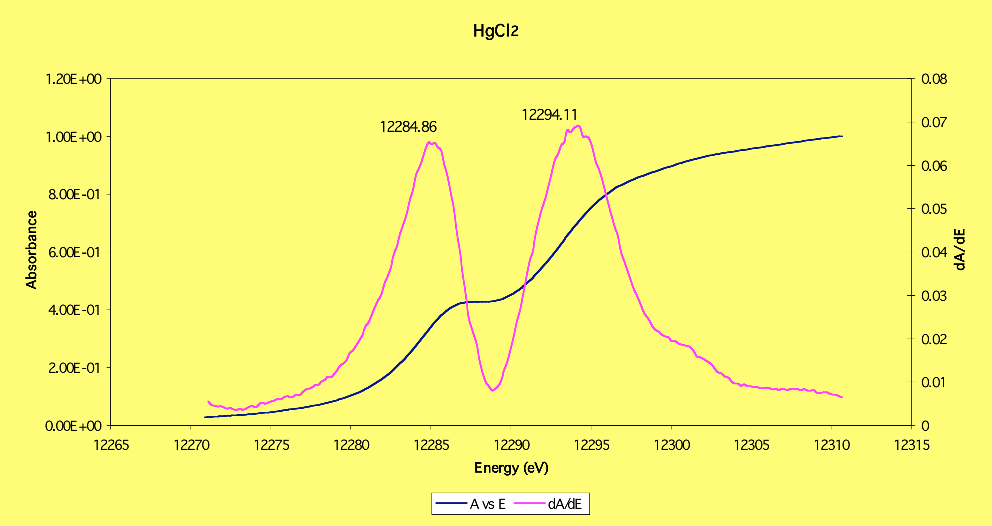
- Excites core electron into unoccupied molecular orbital using X-ray.
- Can be used for solids, liquids, solutions and gases
- Element specific
- X-ray absorption near-edge structure (XANES) can determine oxidation state, speciation
- Extended X-ray absorption fine structure (EXAFS) can determine local atomic environment for the absorbing atoms

Speciation using EXAFS "fingerprinting"



Kim CS, Bloom NS, Rytuba JJ, Brown GE (2003) Environ Sci Technol 37:5102

Hg L-III Edge Spectrum of $HgCl_2$



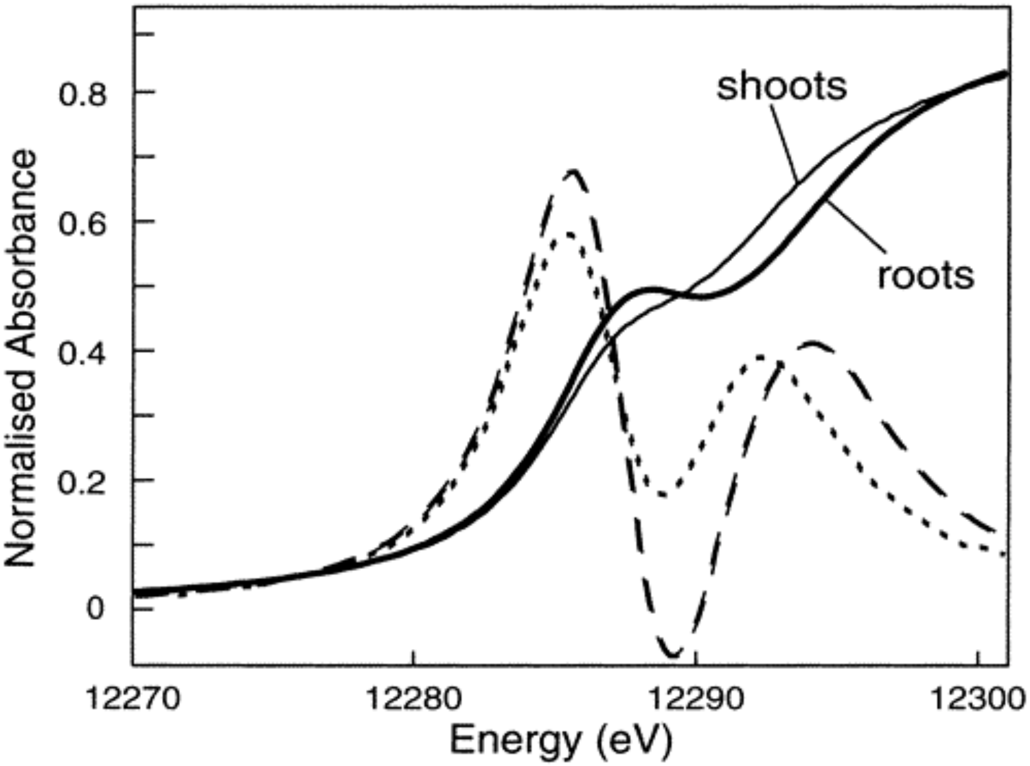
Energy (eV)

Dk Blue: $HgCl_2$ edge

Violet: First derivative

- Hg L3 edge: 2p excitation
- Hg is $[Xe]6s^2 5d^{10}$; Hg(II) loses two 6s electrons
- Allowed transitions $\Delta l = \pm 1$
- Two main transitions: 6s and 6p
- 2p->6p allowed because of mixing of Cl s-orbitals
    - verified with PC Spartan
- Distance between two transitions increases with more ionic bonding

Hg L3 Edges of Hyacinth Roots and Shoots: Initial Speciation using edge inflection points

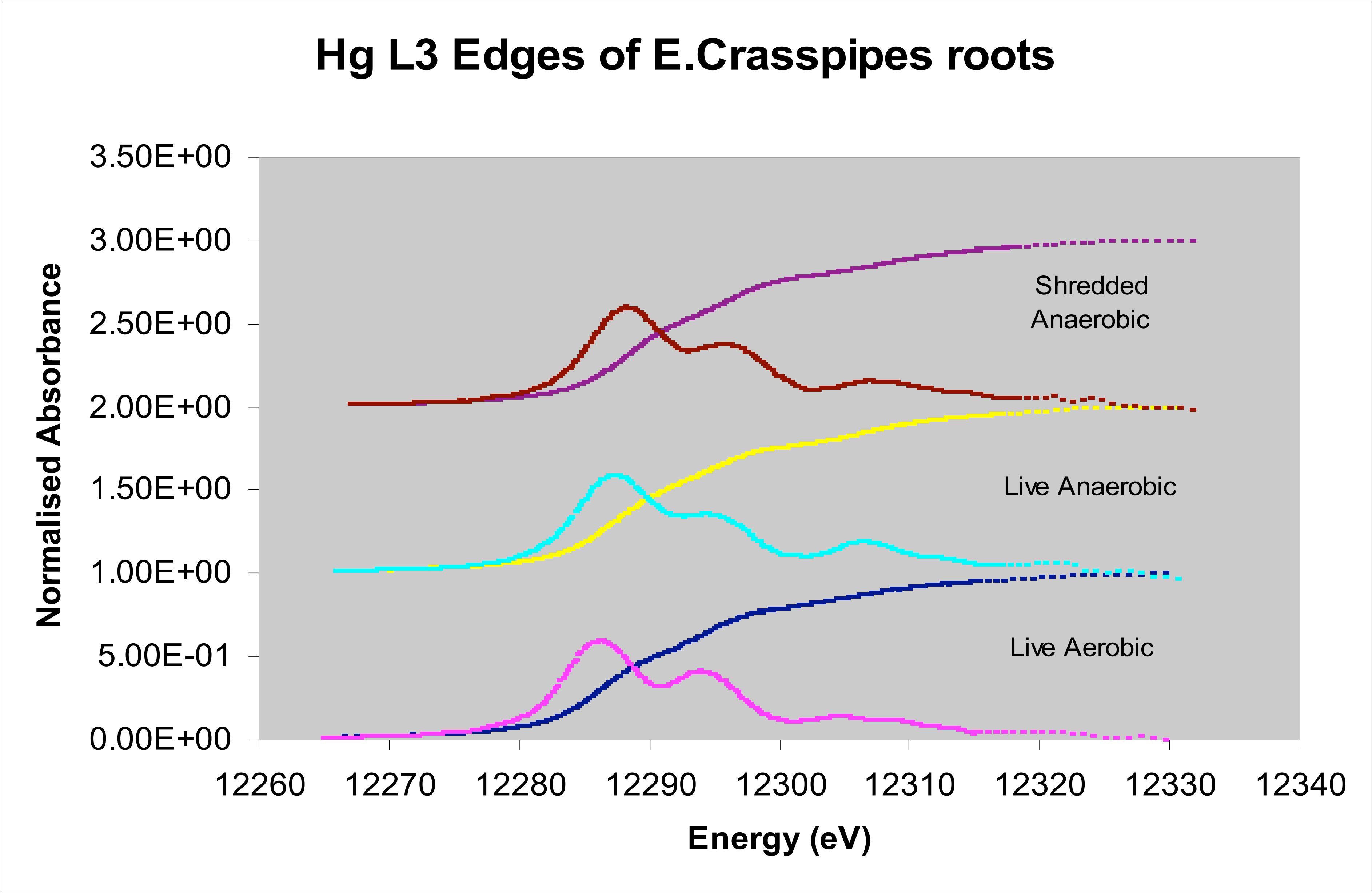


Riddle SG, Tran HH, DeWitt Jg, Andrews JC (2002) Environ Sci Technol 36:1965

Hg L3 Edge Inflection points

Compound	E_1 (eV)	E_2 (eV)	ΔE (eV)
$HgCl_2$	12284.4	12293.2	8.8
$HgBr_2$	12284.2	12292.3	8.1
HgI_2	12285.3	12290.1	4.8
HgO	12283.6	12297.2	13.6
HgS	12284.6	12292.6	8.0
$Hg(Ac)_2$	12285.5	12294.4	8.9
HgThiourea	12284.9	12292.1	7.2
Hg Cysteine	12284.4	12292.6	8.2
Hgdi-cys	12284.6	12292.3	7.7
Hyac. Roots	12284.7	12293.8	9.1
Hyac. Shoots	12285.1	12292.6	7.5

Comparison of shredded/whole plants



Hg L3 Edge Inflection Points

Compound	E1 (eV)	E2 (eV)	ΔE (eV)
Roots Aerobic Live 1	12286.2	12293.9	7.8
Roots Aerobic Live 2	12285.9	12294.0	**8.1**
Roots Anaerobic Live 1	12286.3	12293.6	7.3
Roots Anaerobic Live 2	12286.3	12293.6	7.3
Roots Anaerobic Shredded 1	12286.6	12293.7	7.1
Roots Anaerobic Shredded 2	12286.4	12293.5	7.1
Shoots Aerobic Live	12286.0	12293.0	7.0
Shoots Anaerobic Live	12286.1	12293.0	7.0
Shoots Anaerobic Shredded	12286.0	12293.6	7.6
Dow Sediment	12286.2	12294.1	7.9
$HgCl_2$	12284.6	12292.6	8.0
Hg (Acetate)$_2$	12286.3	12295.7	9.4
Hg Glutamic Acid	12285.3	12299.9	8.6
Hg Methionine	12284.8	12293.4	8.6
Hg Cysteine	12286.2	12293.9	7.7
Hg Dicysteine	12285.8	12293.1	7.3
HgS Wet	12284.4	12298.3	13.8
Methyl HgCl	12286.0	12295.5	9.5
Methyl Hg Glutamic Acid	12286.3	12295.1	8.8
Methyl Hg Methionine	12286.2	12296.0	9.8
Methyl Hg Cysteine	12286.4	12294.1	7.7

Speciation using edge "fingerprinting":

Least-squares fitting of first derivatives of unknowns to model spectra

Growth Conditions	$Hg(Ac)_2$	HgCysteine	HgDicysteine	Methyl HgCysteine
Live, Aerobic	.160 ± .028	.112 ± .036	.690 ± .033	.050 ± .030
Live, Anaerobic	.067 ± .038	.105 ± .048	.694 ± .044	.157 ± .040
Shredded, Anaerobic	.095 ± .049	.099 ± .073	.686 ± .072	.220 ± .064

Summary of Results:

Shredding and methylation of Hg

- Field results:

  -Hyacinth are concentrating mercury compared with water and sediment

- Growth Chamber results:

  - Roots had a greater concentration of mercury than the shoots, and shredded hyacinths had a lower mercury uptake than live hyacinths.

- XAS Results:

  -XAS data revealed that water hyacinth roots undergo speciation changes from a more ionic form in aerobic live plants, becoming more covalent in anaerobic conditions, and more so in shredded plants.

  -Mercury methylation increases from about **5%** in live, aerobically grown plants to **15.7%** in live plants grown anaerobically, to **22%** in shredded plants grown anaerobically

Conclusions:

- Shredding of hyacinths
  - Increases the amount of organic matter
    - Can decrease oxygen content
    - DO was increased at Dow Wetlands, decreased in Lambert Slough after shredding
  - Can increase methylmercury production

- We should continue to explore alternative routes for removal of water hyacinths from the Delta waterways
  - Possibility: Mechanical removal
    - Side effect: Hg removed as well

- This is strongly relevant to the understanding of the role of organic matter in mercury methylation, and the CALFED goal of remediation of mercury, and minimizing mercury methylation in the Delta.

Future Work

- Hg uptake by *Spartina foliosa, S. alternaflora*
- Hg studies in fish, hair
    - Total Hg, possibly speciation

Acknowledgements

- Students:

Michael Rajan

Mike Hua

Jeannine Darrow

Miguel Mendoza

Adam Hackett

- Colleagues

Jane DeWitt, SFSU

Ben Greenfield, SFEI

- CALFED
- SFEI
- CAL DBW
- CSU East Bay
- SSRL/DOE