Validation of Diffusive Gradient in Thin-films Technique for Mercury and Methylmercury Measurements in Natural Environments

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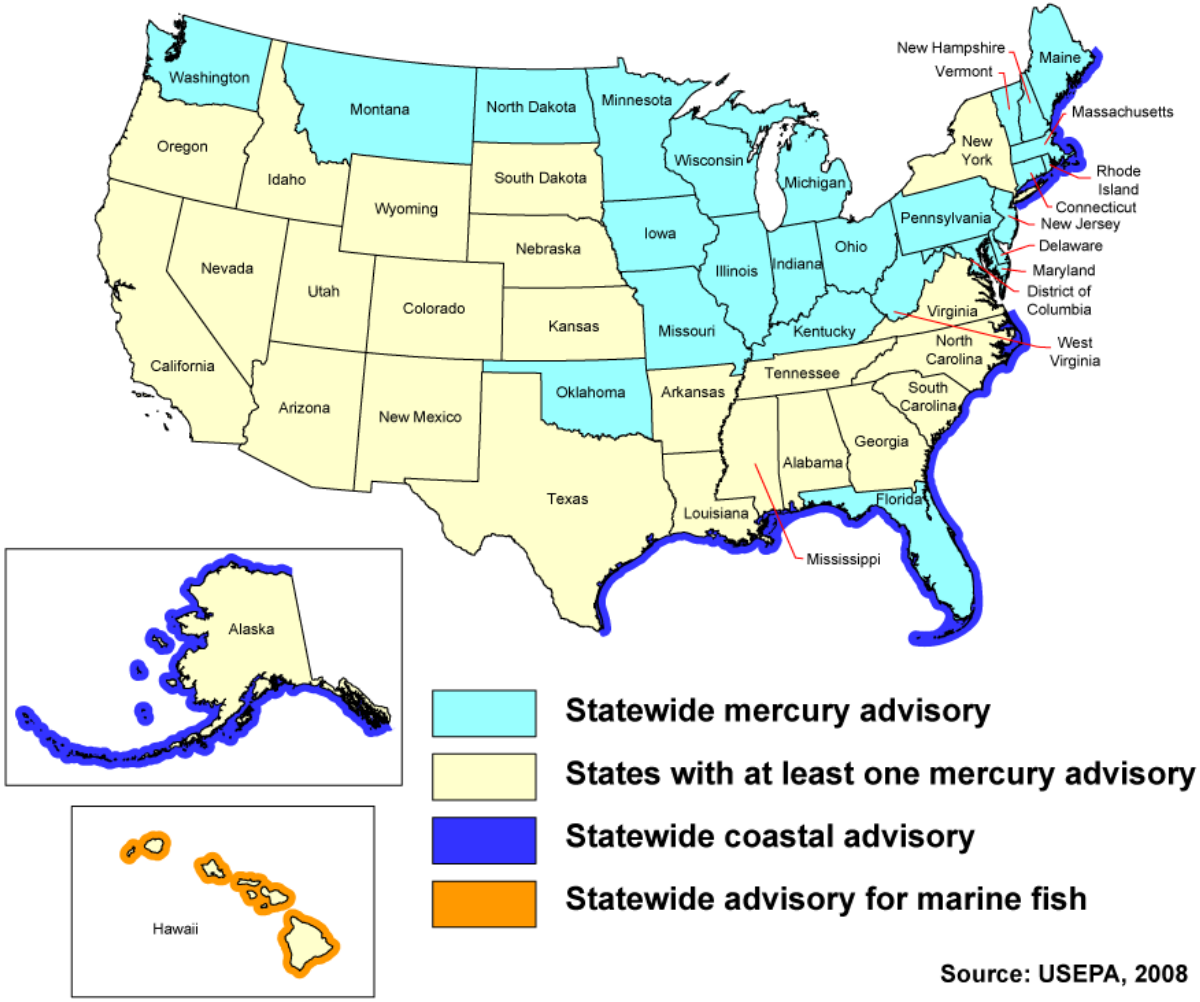
Outline

- Background and Theory
- General DGT fabrication
- Laboratory Experiments - Validation
  - Resin performance
  - Sorption and Elution efficiency studies
  - Analytical limitations
  - Optimization

Mercury and Methylmercury

- Mercury is a pollutant of global concern
  - Globally ubiquitous and environmentally persistent
  - Highly toxic
- Toxic effects in humans and wild life
  - Neuro-developmental effects (MeHg)
  - Coronary heart disease
  - Kidney damage (Hg)
- Highly bioaccumlative
- EPA Ambient Water Quality Criteria (AWQC) 2001
  - 0.3 mg MeHg per kg fish, wet

Motivation: Fish consumption advisories in the US



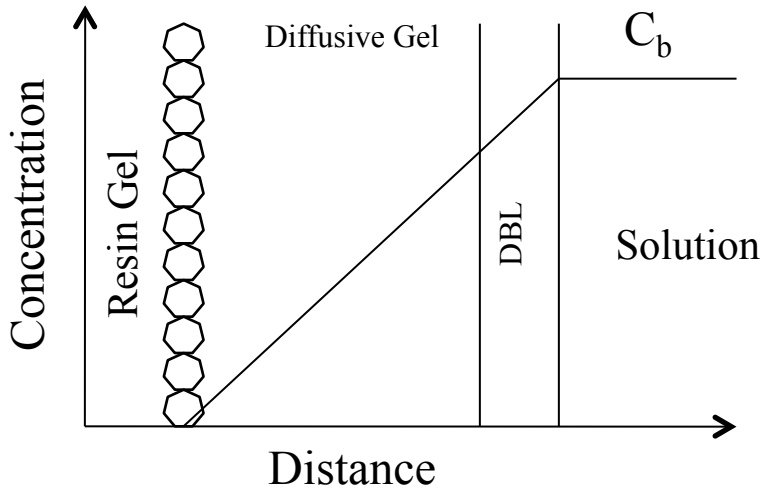
http://animalblawg.files.wordpress.com/2010/03/mercury-warning2.jpg

Diffusion Gel Thin Film (DGT) background

- Davison & Zhang – Lancaster, UK
- Based on Fick's 1st Law of Diffusion
  - Measures flux, not an equilibrium device

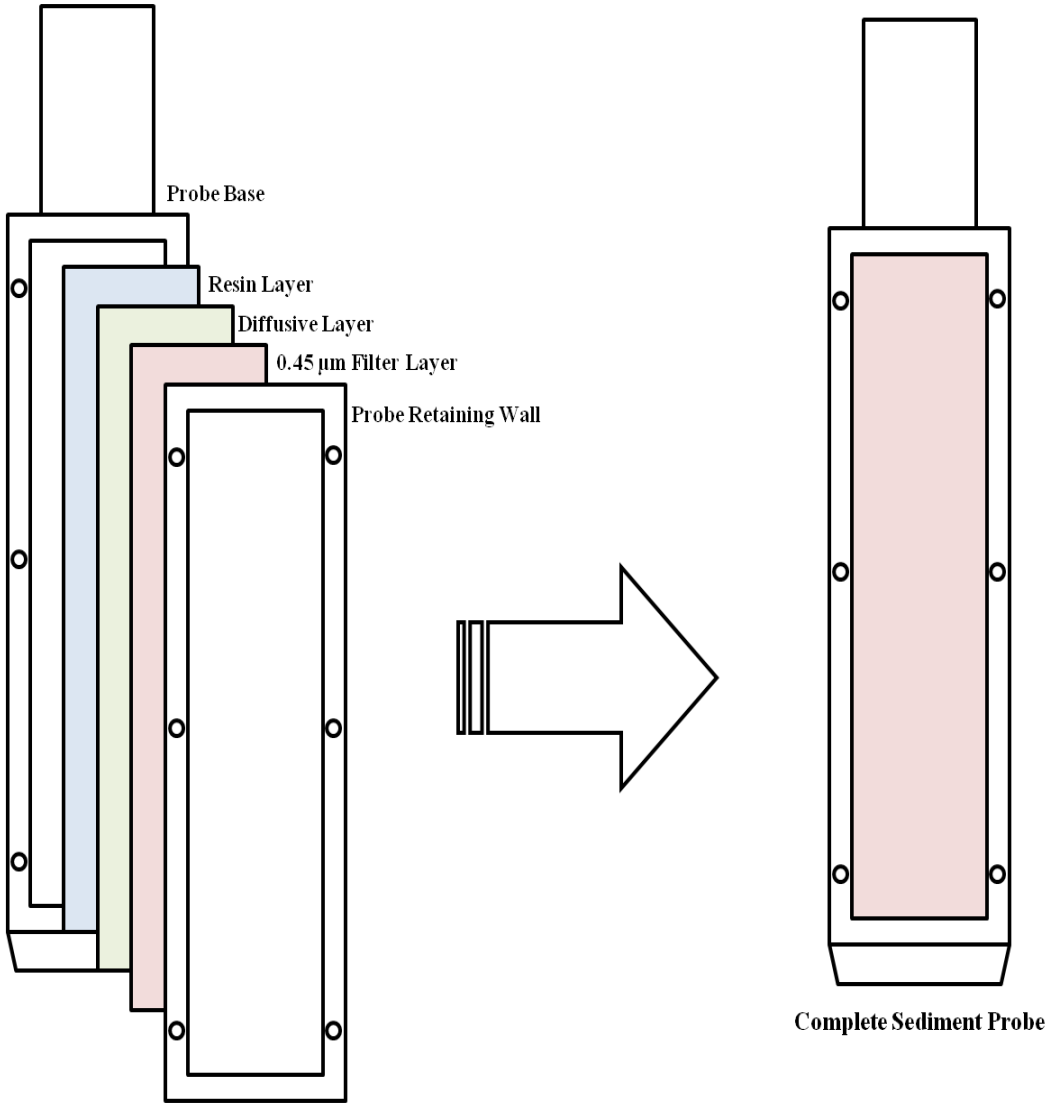
$$J = -D\frac{\partial \varphi}{\partial x} \Rightarrow J = \frac{DC_b}{\Delta g} \Rightarrow C_b = \frac{M\Delta g}{DtA}$$

- Diffusion of metal = to that in pure water

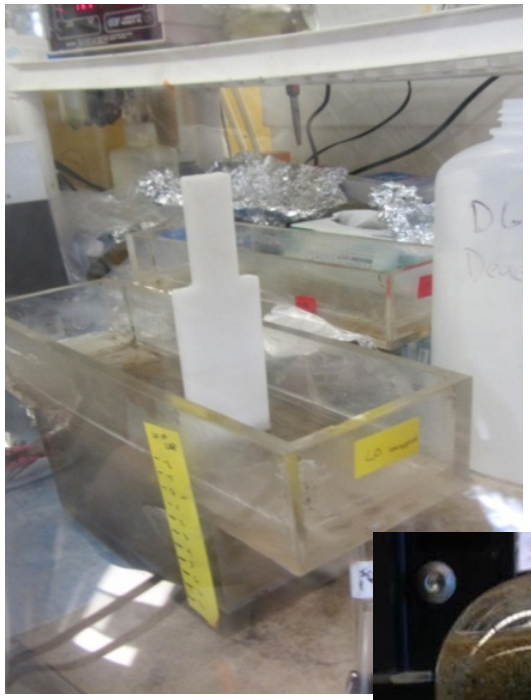


Diffusion Gel Thin Film (DGT) Device Conventional

- Resin
  - Chelex 100
  - Acrylamide gel base
- Diffusion layer
  - Acrylamide gel



Application of DGTs for in-situ measurements as monitoring tool



Goals

- DGT is applied for in-situ measurements of surface water and porewater concentrations
  - Mercury 10-100000 ng/L
  - Methyl mercury 0.1-10 ng/L

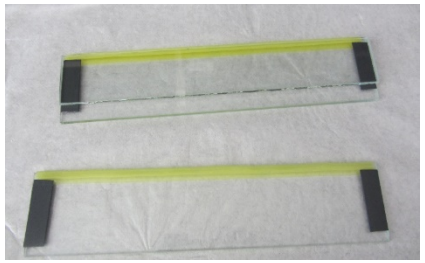
➢ Evaluate resin material

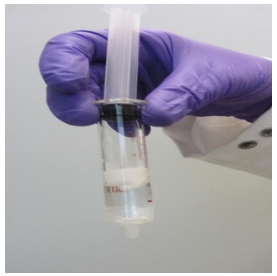
➢ Optimize elution condition to validate reliable measurement of mercury and methyl mercury

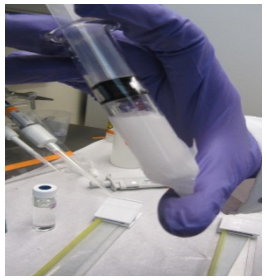
➢ Evaluate matrix effects and analytical challenges

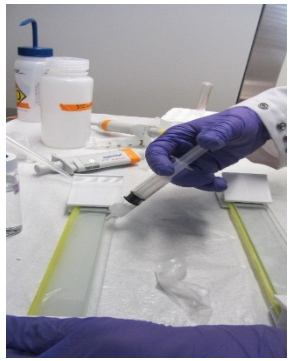
DGT preparation

Casting

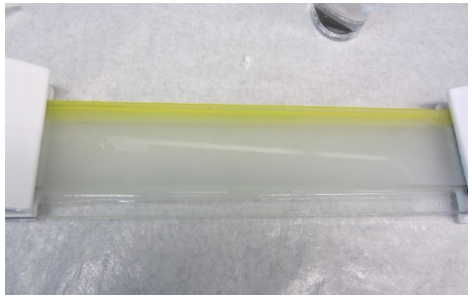


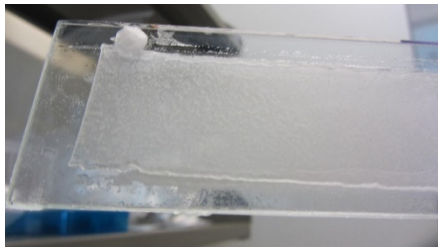






Settling





Hydration

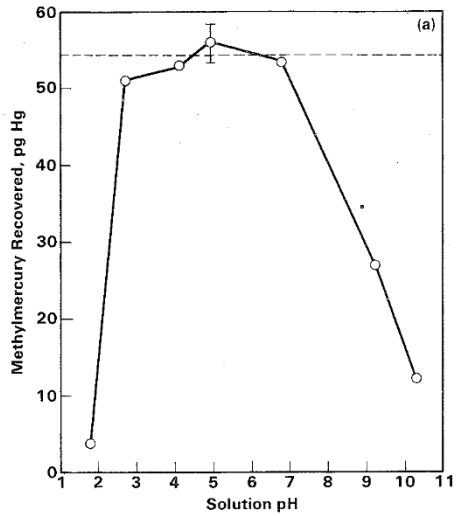
Construction

DGT Procedure

- DGT are fabricated in house
- Deployed in natural systems for ~2-7 days
- Analysis performed
  - Depth profilers sectioned at 2cm intervals
  - Resin split for TotHg/MeHg
  - TotHg resin is eluted in HCl and analyzed by EPA 1631 (Oxidation (BrCl)/Reduction/CVAFS)
  - MeHg resin is eluted in HCl/Thioreau and analyzed by EPA 1630 (Ethylation/Purge &Trap/GC-separation/ CVAFS)

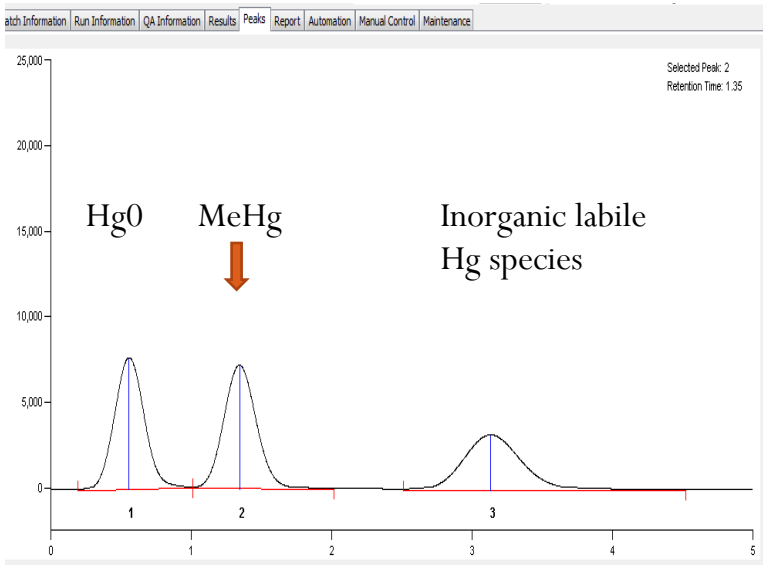
MeHg analysis by EPA method 1630

Ethylation - Purge &Trap/Thermal desorption - GC-separation and cold-vapor atomic fluorescence spectrometry (CVAFS)



Effect of pH

Bloom 1989, Can. J. Fish. Aquat.Sci, Vol.46



Merx, Brooksrand

DGT for mercury measurements

Resin	Analyte	Matrix	Uptake range	Detection	Author
Chelex 100	Hg	NaCl HA, pH 6-8	0.6-3 mg/L	AAS	Divic et al.2010, Cent.Eur.J.Chem. 8(5), 1105.
Speron Thiol	Hg	NaCl, HA, pH 2-8	0.6-3 mg/L	AAS	Divic et al.2010
Duolite GT73	Hg	NaCl, HA pH 2-10	0.6-3 mg/L	AAS	Divic et al.2010
3-Mercapto-propyl functionalized silica gel – 3MSH	Hg, MeHg	Oxic surface water, pH 8	20 – 2000 ng/L	IC-ICP-MS	Hong et al. 2011, ES&T, 45, 6429.
3MSH	MeHg	Coastal seawater, pH range: 3-9	1 – 500 pg	CVAFS or Isotope dilution	Clarisse and Hintelmann 2006, J. Environ. Monit., 8, 1242.

Laboratory Validation Experiments

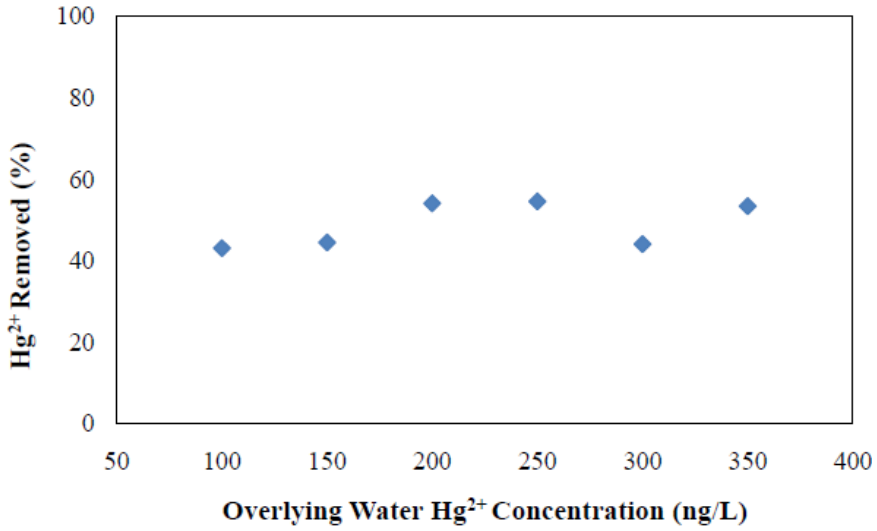
- Sorption Experiments
  - Evaluated after 24 hr equilibrium while in end-over-end tumbler
  - 25 - 700 ng/L Hg^{2+} concentrations
  - 10 – 500 ng/L MeHg concentration
- Extraction Efficiency Experiments
  - Resin disk – preloaded or directly spiked – with MeHg/Hg
  - Eluted with acidic thiourea solution/HCl for 24 h in the dark

Mercury Resin Evaluation

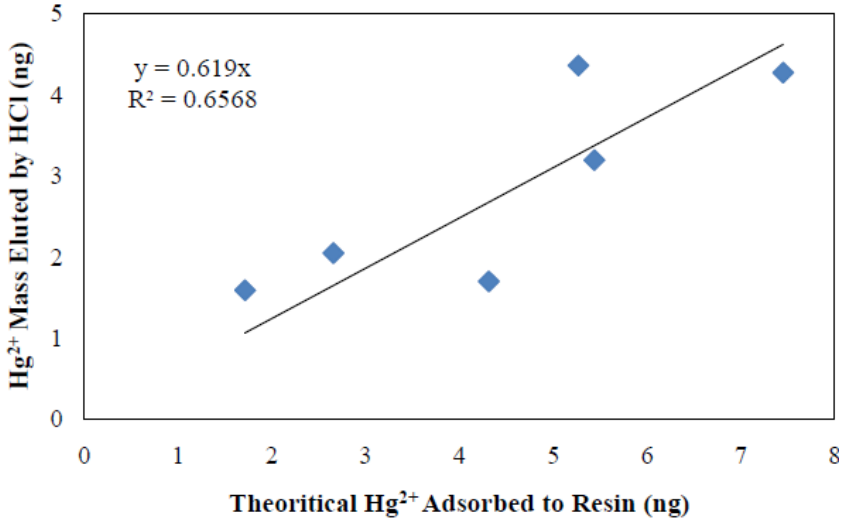
- Chelex-100
  - Poor Hg sorption capacity
- Spheron Thiol
  - Excellent resin for Hg, but no longer manufactured
- Lewatit Monoplus TP-214
  - Inability to form gel (setting time up to 6h)
- Ambersep GT74 resin
- 3-Mercaptopropyl Functionalized Silica Gel (3-MSH)

Laboratory Experiments – Ambersep GT74

Sorption efficiency

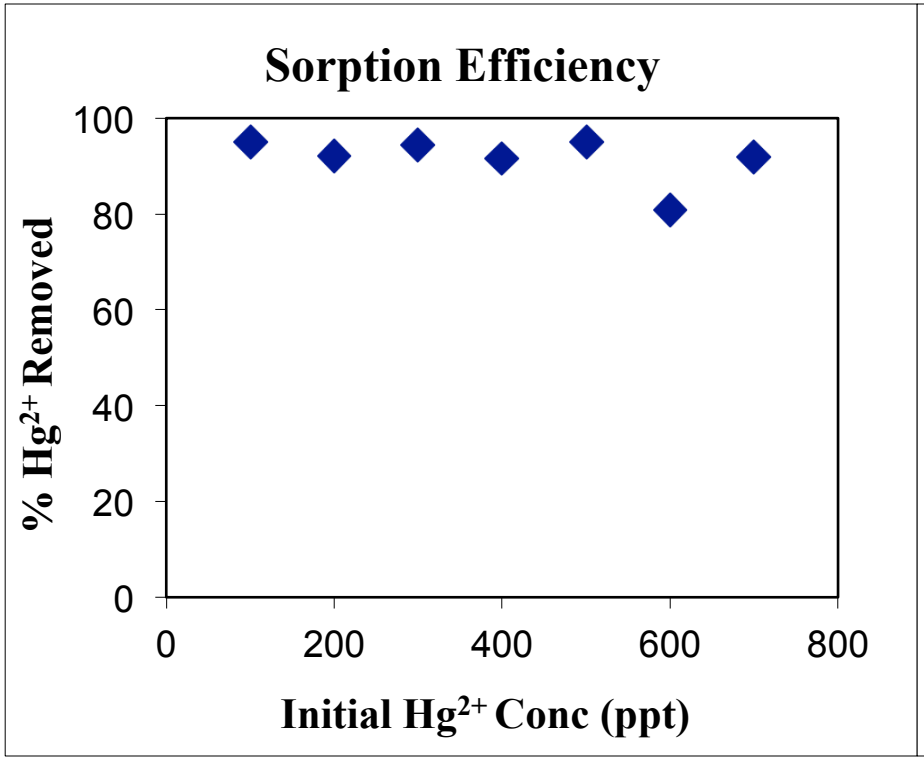


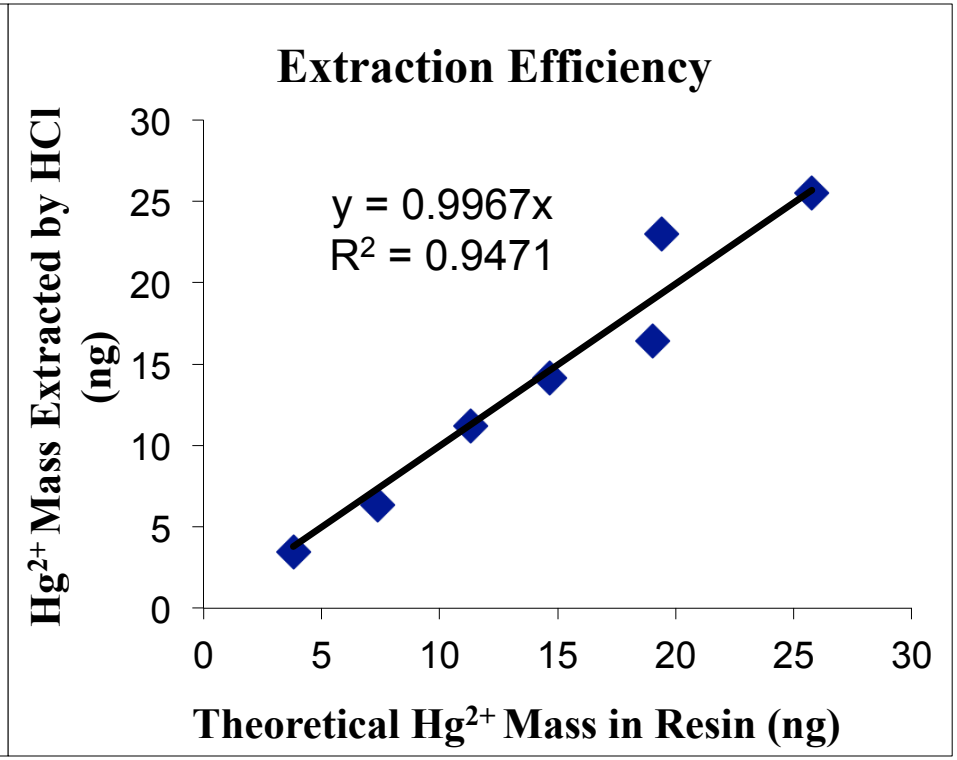
Elution efficiency



50% average Hg sorption
61% average Hg extraction efficiency w/ HCl

Laboratory Experiments THg (3-MSH)





92% average Hg sorption

96.5% average Hg extraction efficiency w/ HCl

Mercury Resin Evaluation

- Chelex-100
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- Spheron Thiol
  - Excellent resin for Hg, but no longer manufactured
- Lewatit Monoplus TP-214
  - Inability to form gel (setting time up to 6h)
- Ambersep GT74 resin
  - Poor Hg sorbing capacity and extraction efficiency
- 3-Mercaptopropyl Functionalized Silica Gel (3-MSH)
  - Good results for Hg

Ambersep GT74

3-MSH

Evaluation of 3-MSH resin from different suppliers – THg background

	Resin as received		Resin disk	
resin supplier	**mTHg /100mg beads (pg/mg)**	**SD**	**mTHg in a resin disk (pg)**	**SD**
Biotage Isolute - batch 1	61	18	96.2	19.3
Biotage Isolute - batch 2	70		112.2	52.4
Biotage Isolute - batch 3	96	59		
Biotage Isolute - batch 4	55	30		
Sillicylce Batch 1	737	484		
Sillicylce Batch 2	4904	675		
Sigma Aldrich	28	14	130	24

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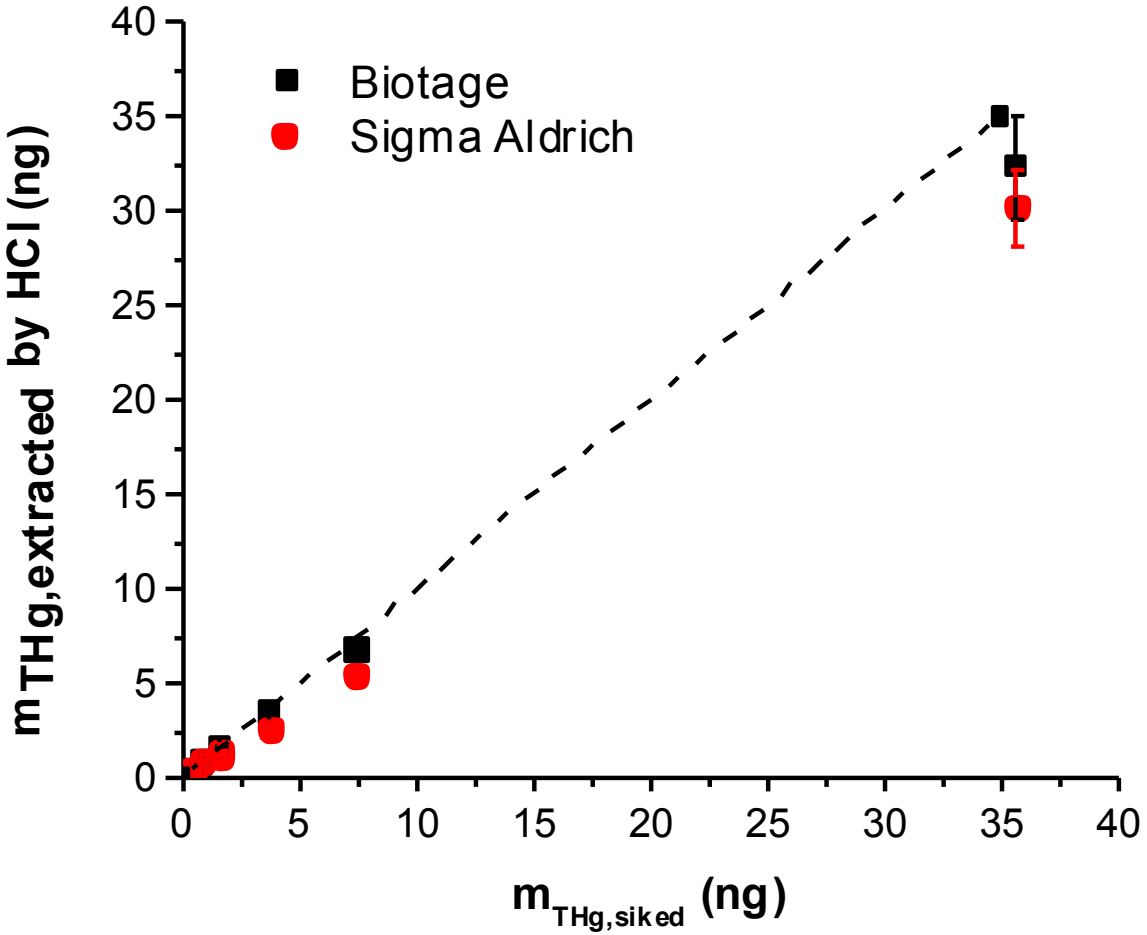
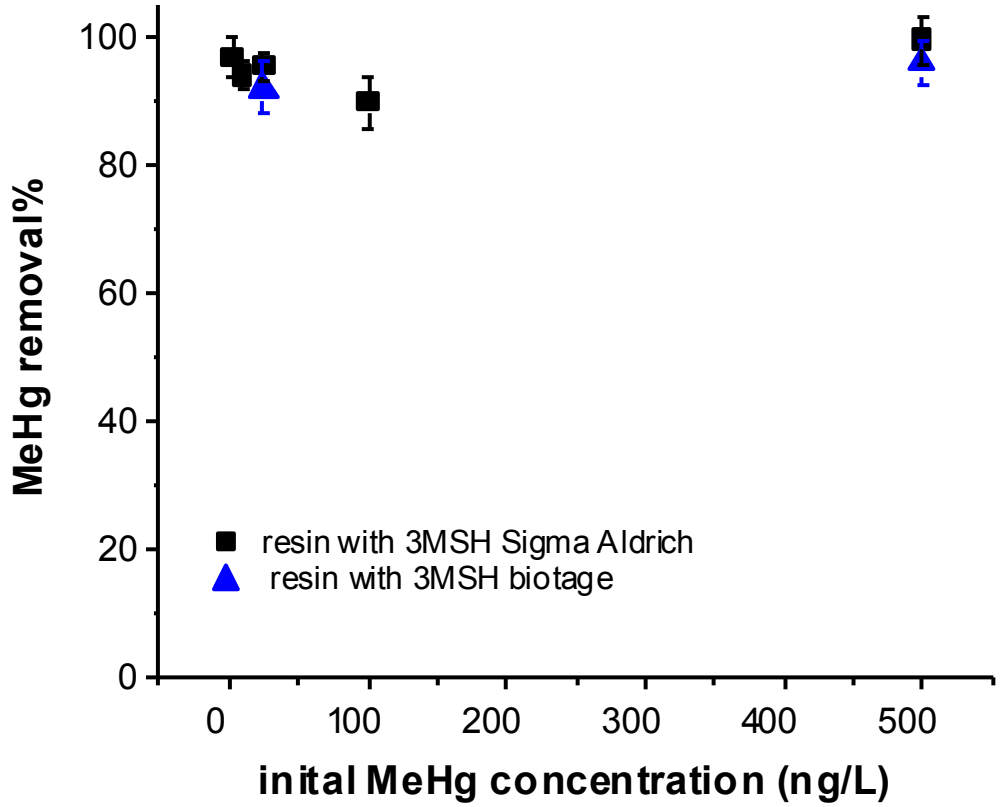


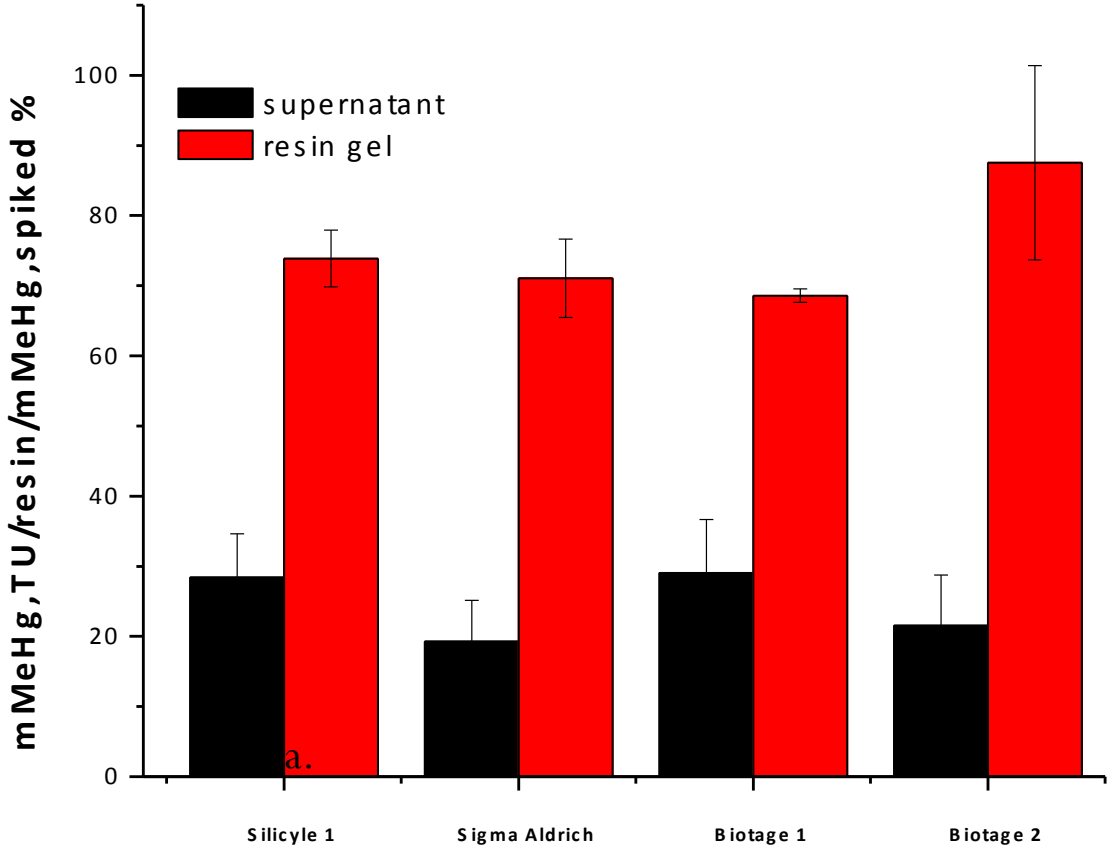
Sorption efficiency of MeHg on 3-MSH resin gel layer



10 mM $NaNO_3$ pH 7.5, t=24 h, A=3.14cm^2

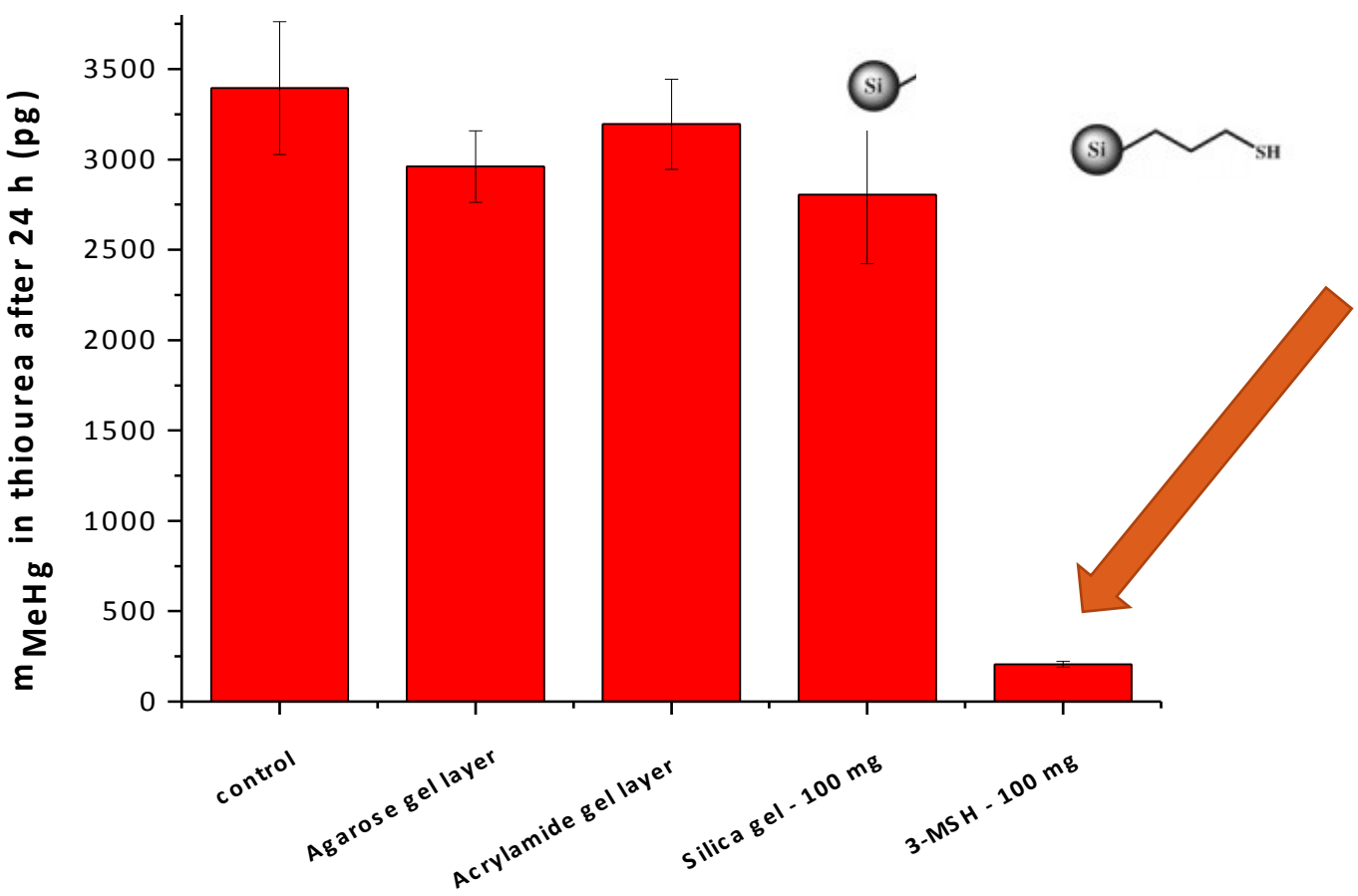
Evaluation of 3-MSH resin from different suppliers - MeHg Extraction efficiency

Elution condition: $m_{MeHg,spiked}$=1000pg, 3 ml 1.3 mM thiourea 0.1 M HCl, t=24h dark



Partitioning of MeHg on 3-MSH in acidic thiourea – DGT components

1.3 mM thiourea 0.1 M HCl, t=24h dark

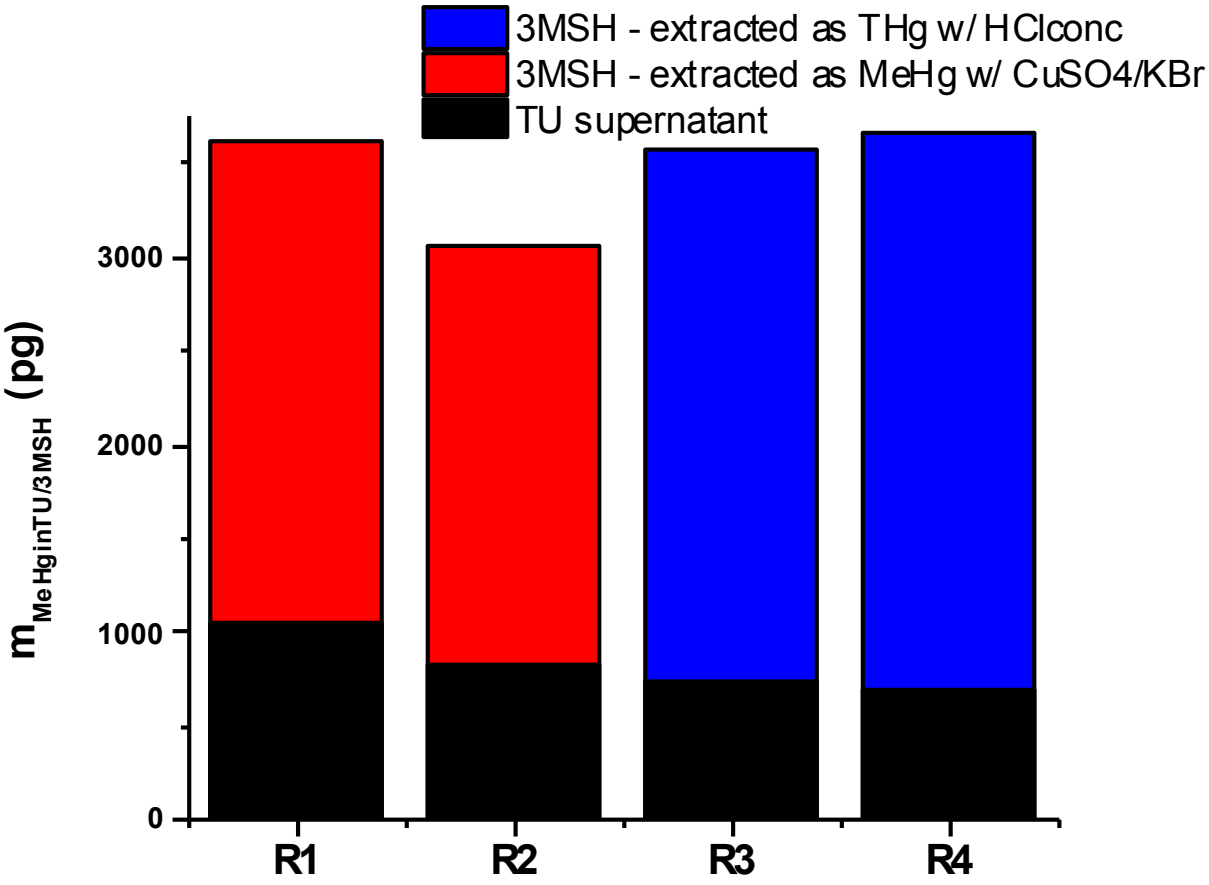


Diffusive Layer Resin Layer

➔ MeHg is complexed by the thiol-resin

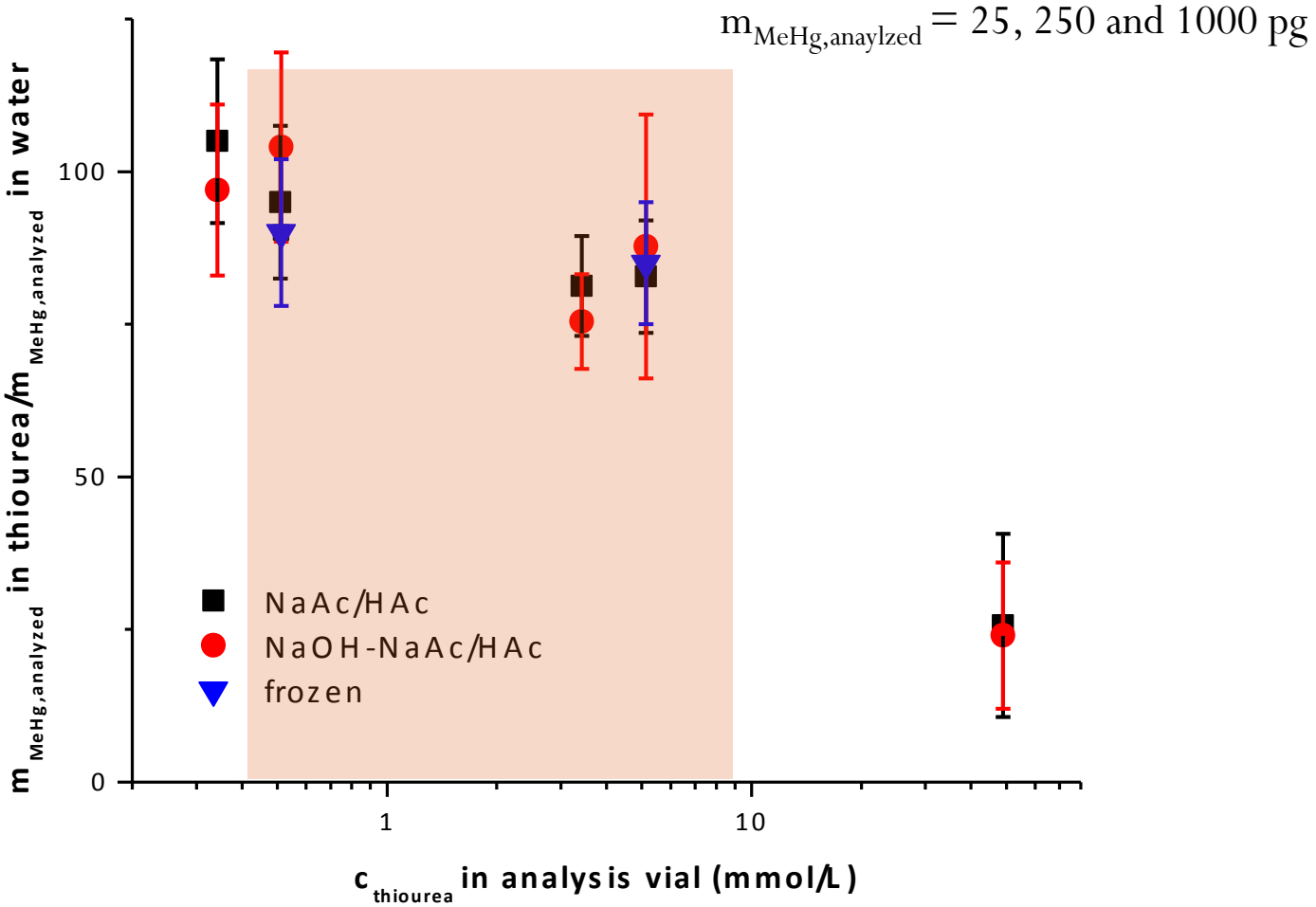
Partitioning of MeHg on 3-MSH in acidic thiourea - speciation

100 mg 3-MSH, $m_{MeHg,spiked}$=4000pg, 15 ml 1.3 mM thiourea 0.1 M HCl, t=24h dark

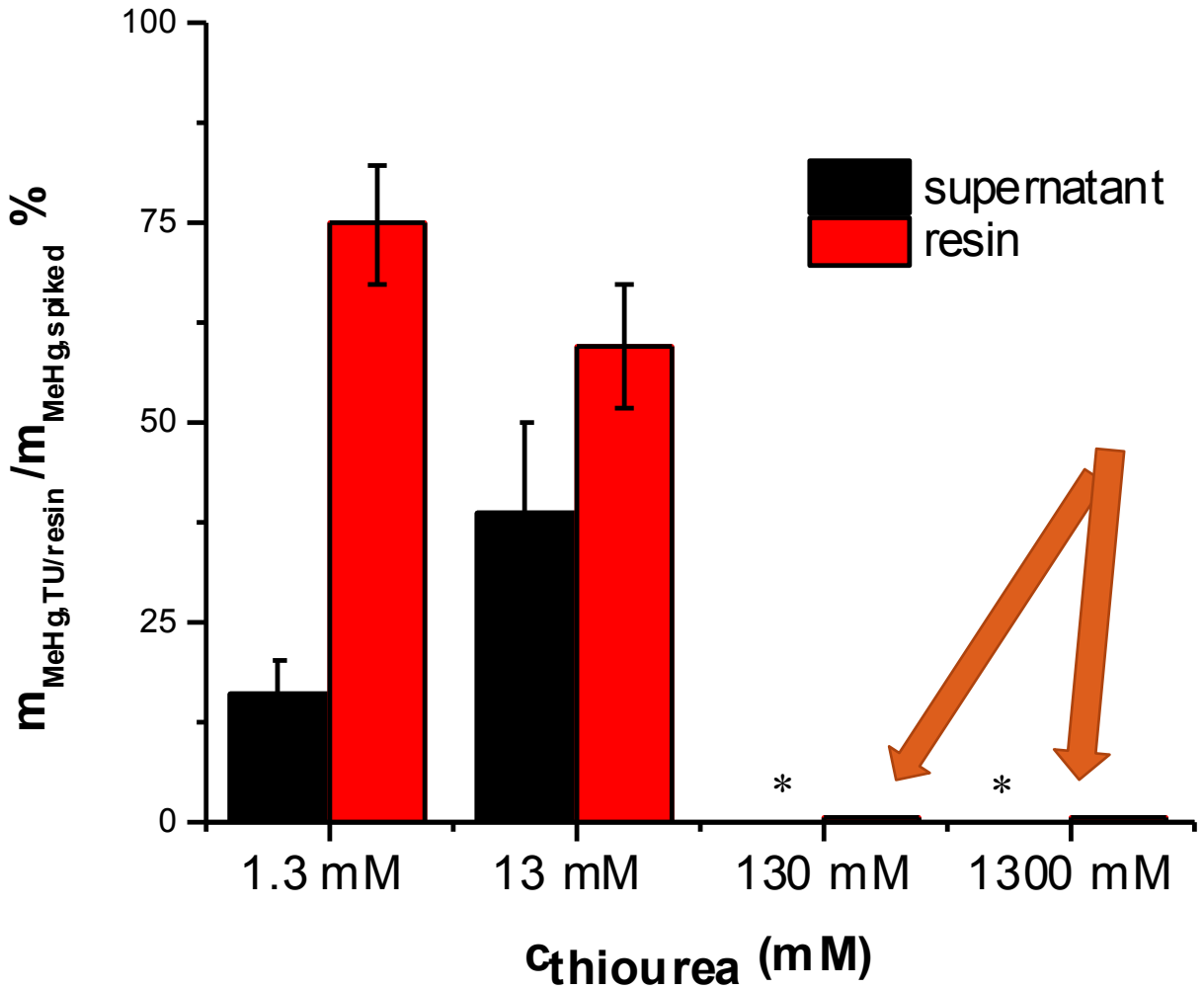


➔ Speciation is preserved

Matrix effects of thiourea on MeHg analysis



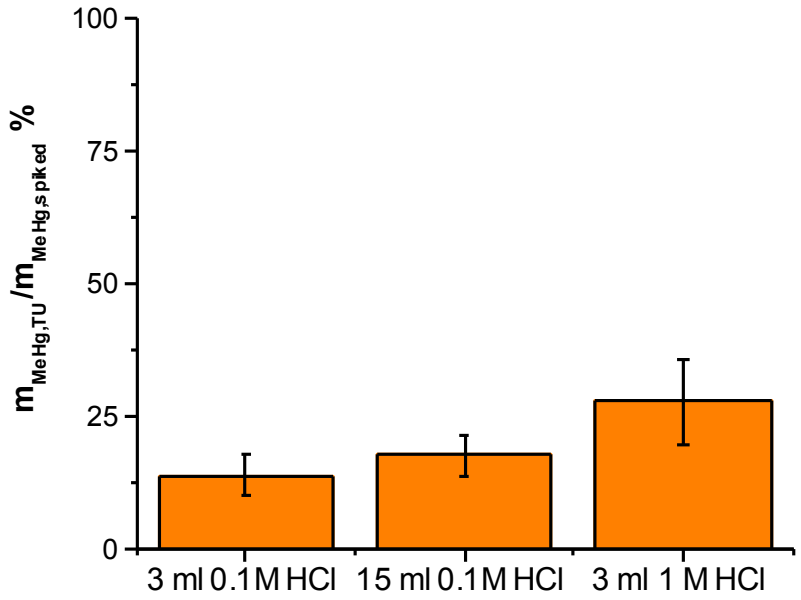
Optimization of elution efficiency – Thiourea concentration



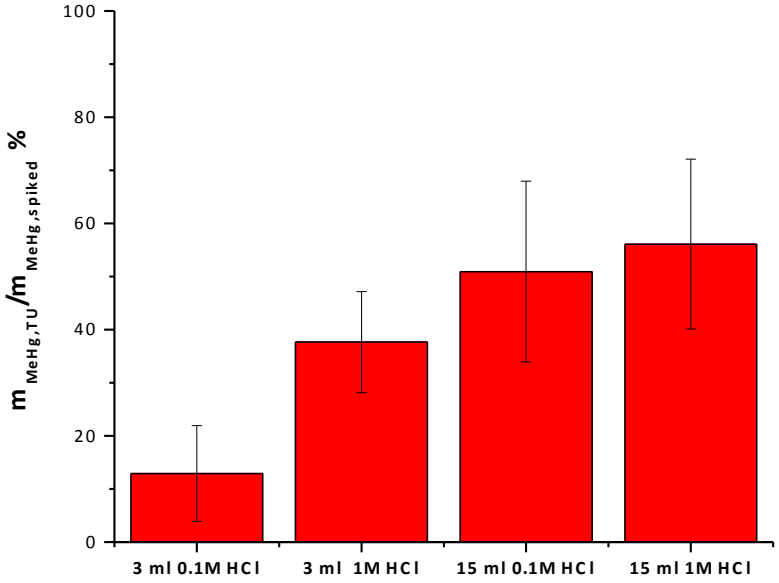
Analytical issues – matric effect

Optimization of elution efficiency – Thiourea volumen and HCl concentration

1.3 mM thiourea



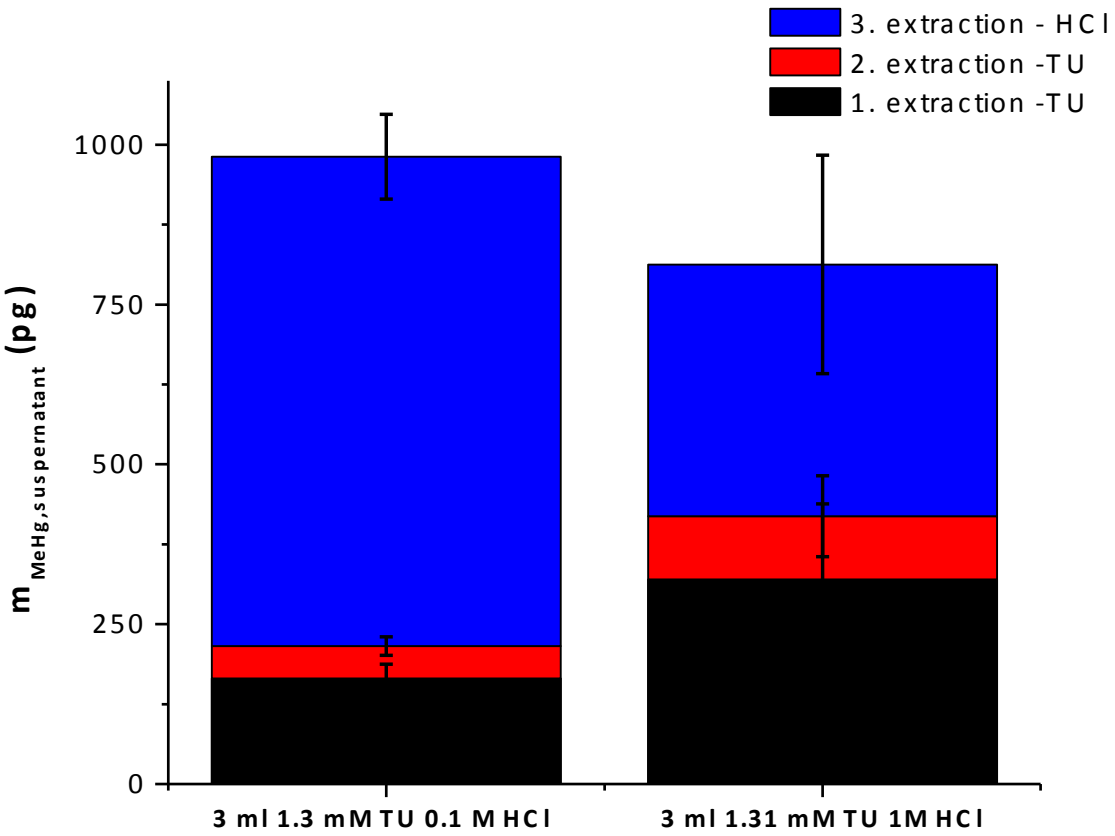
13 mM thiourea



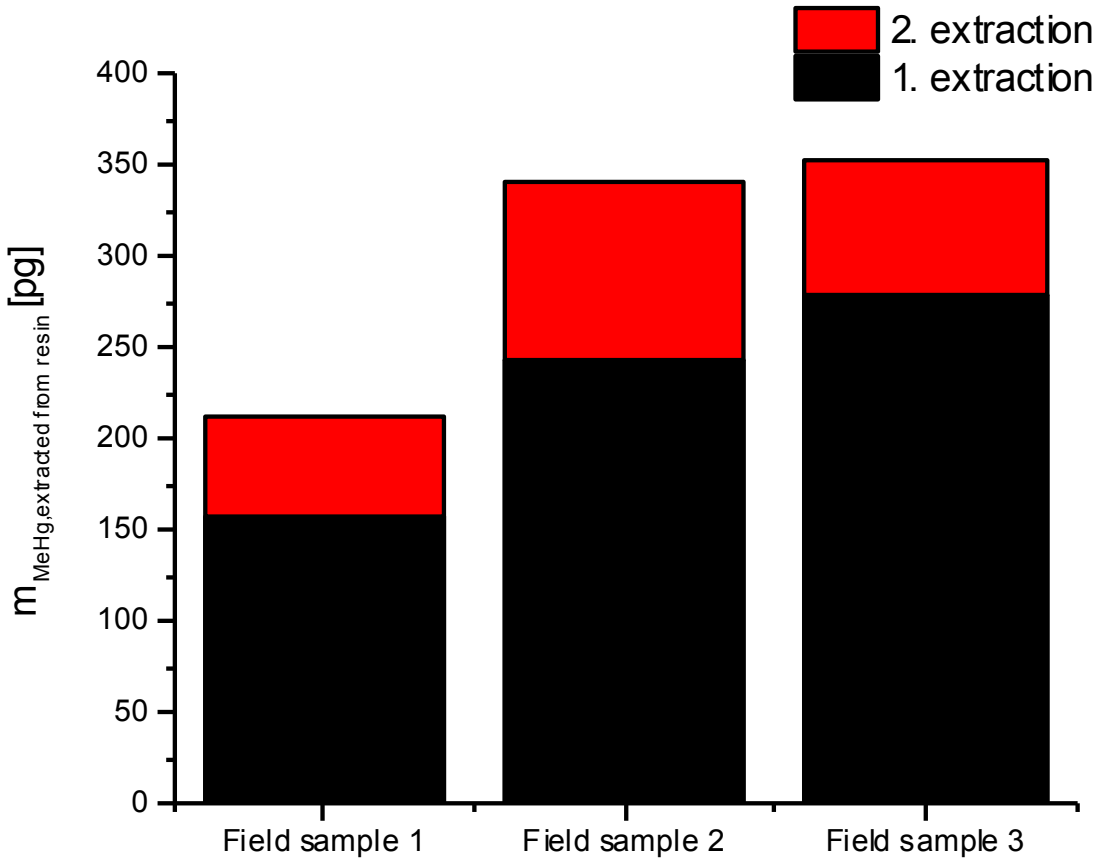
m_{MeHg}=1000pg, t=24h dark

Optimization of elution efficiency – Sequential extraction

1. Step: Resin disk was spiked with 1000 pg MeHg
2. Step: Resin disk was eluted with 3 ml 1.3 mM thiourea 0.1mM HCl (2 times)
3. Step: Resin disk was eluted with HCl



Sequential extraction – field samples



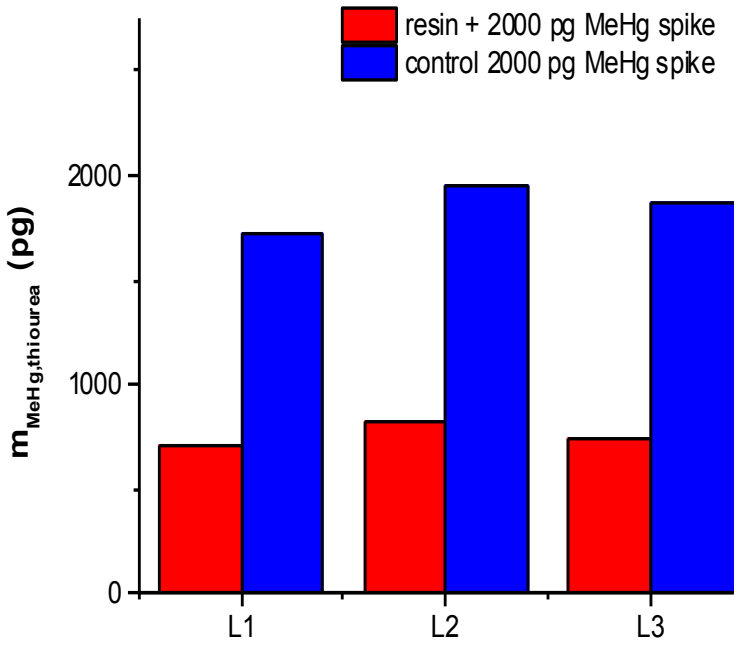
Elution condition: 15 ml 13.1 mM thiourea 0.1 M HCl (2 times)

Field samples – Matrix spike recovery

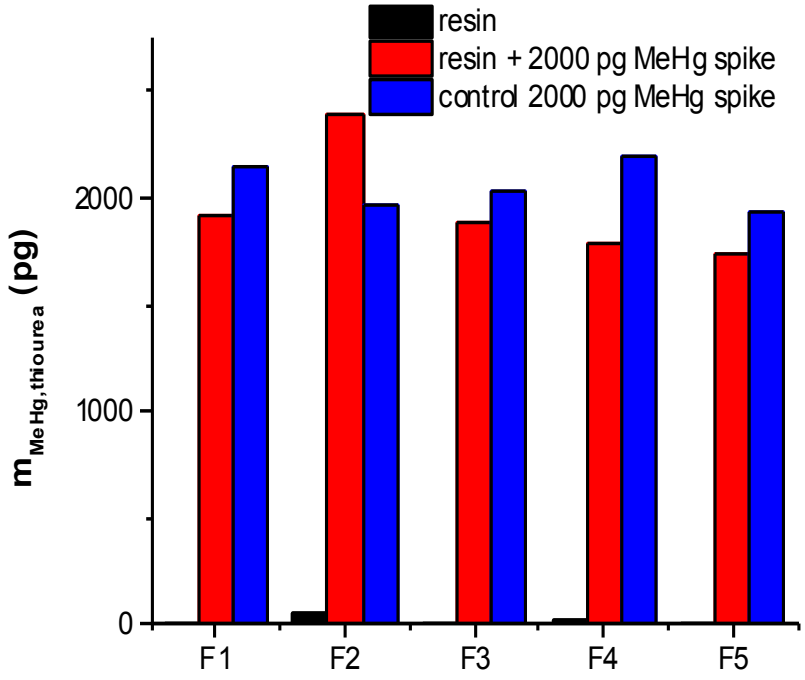
Field deployment: DGT was deployed in Hg-impacted river sediment for 48 h

Lab: Resin was spiked with 2000 pg MeHg and eluted with 15 ml 13 mM thiourea 0.1mM HCl for 24h

"clean" resin – as prepared

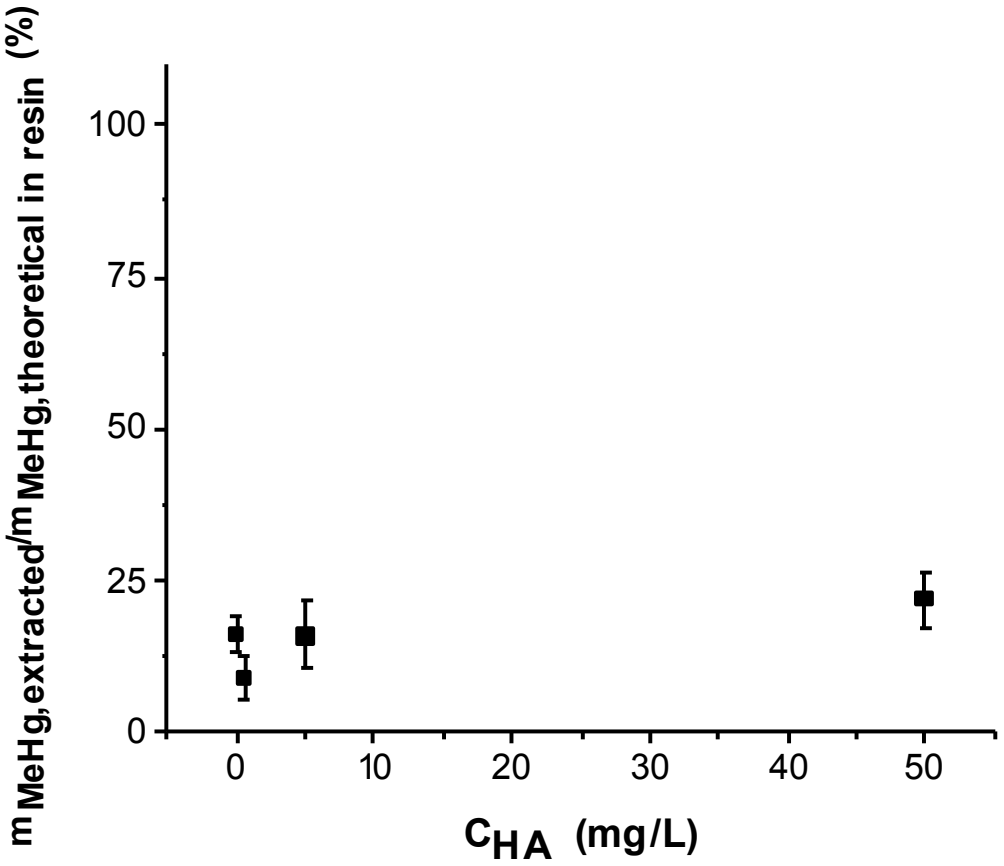


Sediment exposed resin



Effect of natural organic matter

1. Step: Resin disk was equilibrated in buffer: 15 ng/L MeHg 10mM $NaNO_3$ c_{HA} = 0 – 50 mg/L
2. Step: Resin disk was eluted with 3 ml 1.3 mM thiourea 0.1mM HCl



Conclusions

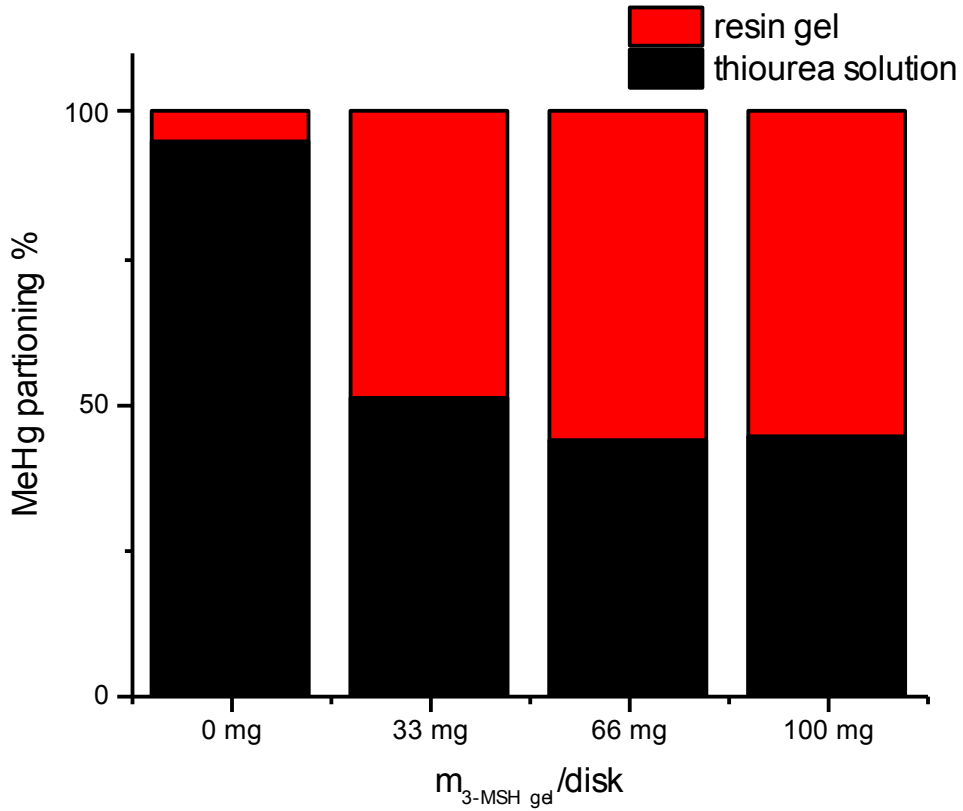
- 3-MSH demonstrates affinity for Hg and MeHg, has a high extraction efficiency for THg, and is compatible with the gel making process
  - Hg: 92% average Hg sorption and 96.5% average Hg extraction efficiency w/ HCl
  - MeHg: 90% average MeHg sorption and 50 % average MeHg extraction efficiency w/ acidic thiourea
- Demonstrates potential of resin for *in-situ* Hg/MeHg detection
- Further evaluation of matrix effects needed
  - Matrix species should be performed on real samples

Thank you

- Dr. Reible Research group at TTU and UT Austin
  - Tea Vtlar and Taryn Tiggers, UT Austin
  - Elaine Hung and Mwale Chiyenge, TTU
- Julian Merz and Joel Creswell, Brooks Rand Instruments
- You for your kind attention

Partitioning of MeHg in acid thiourea – Effect of 3-MSH mass in the gel layer

1.3 mM thiourea 0.1 M HCl



m_{MeHg}=1000pg, t=24h dark