Gellyfish:

An In-Situ Equilibrium-Based Sampler for Determining Multiple Free Metal Ion Concentrations in Aquatic Systems

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Outline

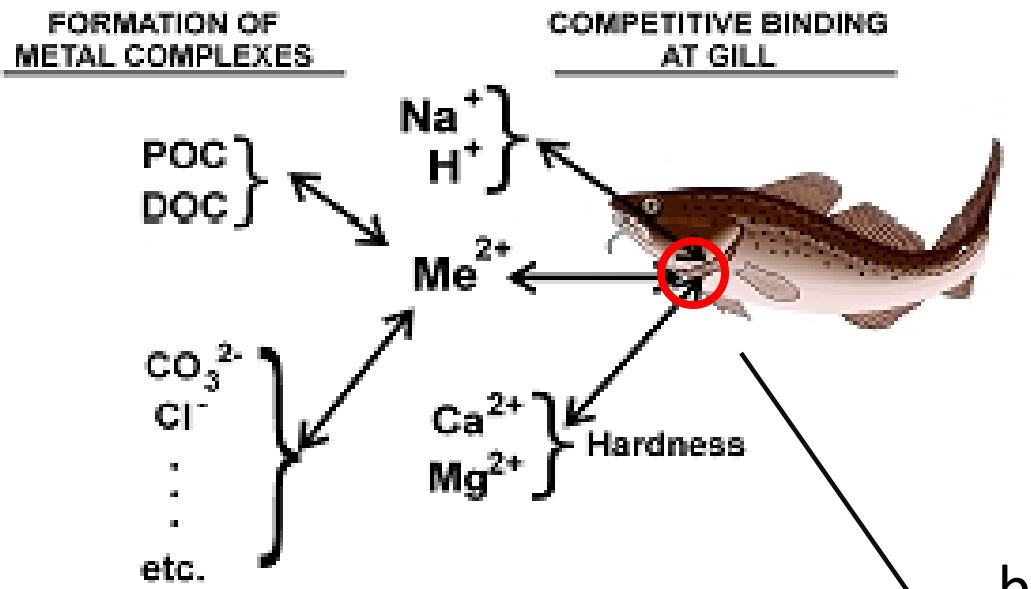
- Introduction & Background
- Major features of the Gellyfish
  - Design & structure
    - Preparation
    - Laboratory validations & tests
    - Correlation with biomonitors
    - Reusability & cost
- Applications
  - Case I: Spatial & temporal measurements of free metal ions in Boston Harbor
  - Case II: Metal-specificity of natural organic ligands

Why do we need the Gellyfish?

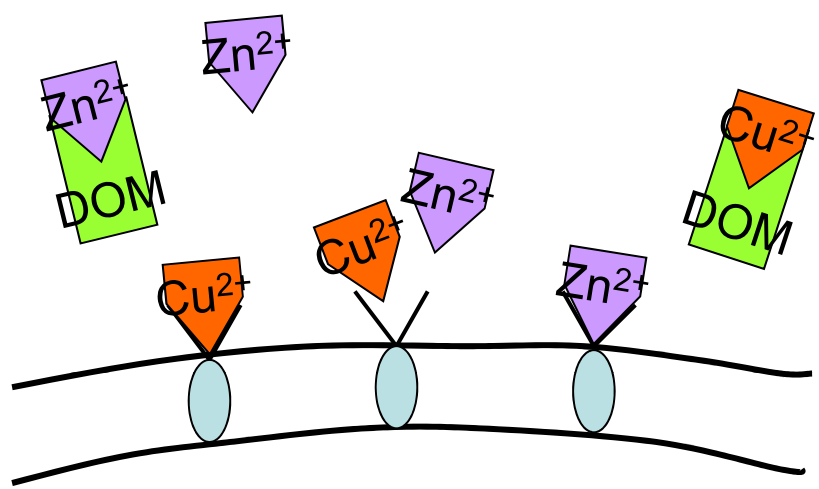
- Importance of metal speciation
  - Controls bioavailability, transport & fate
  - Free ions can be as low as <0.1% of the total
  - This fraction varies in space & time
  - Typical concentration in water: pM ~ nM
  - Focus of new generation EPA water quality criteria

- Current techniques to determine Me^{2+}:
  - ASV, CSV, ISE, DGT, etc.
  - Labor-intensive, expensive, requires experience
  - Can measure ONE metal at a time
  - Gellyfish: an inexpensive, rapid, in-situ, equilibrium-based, multi-metal sampler

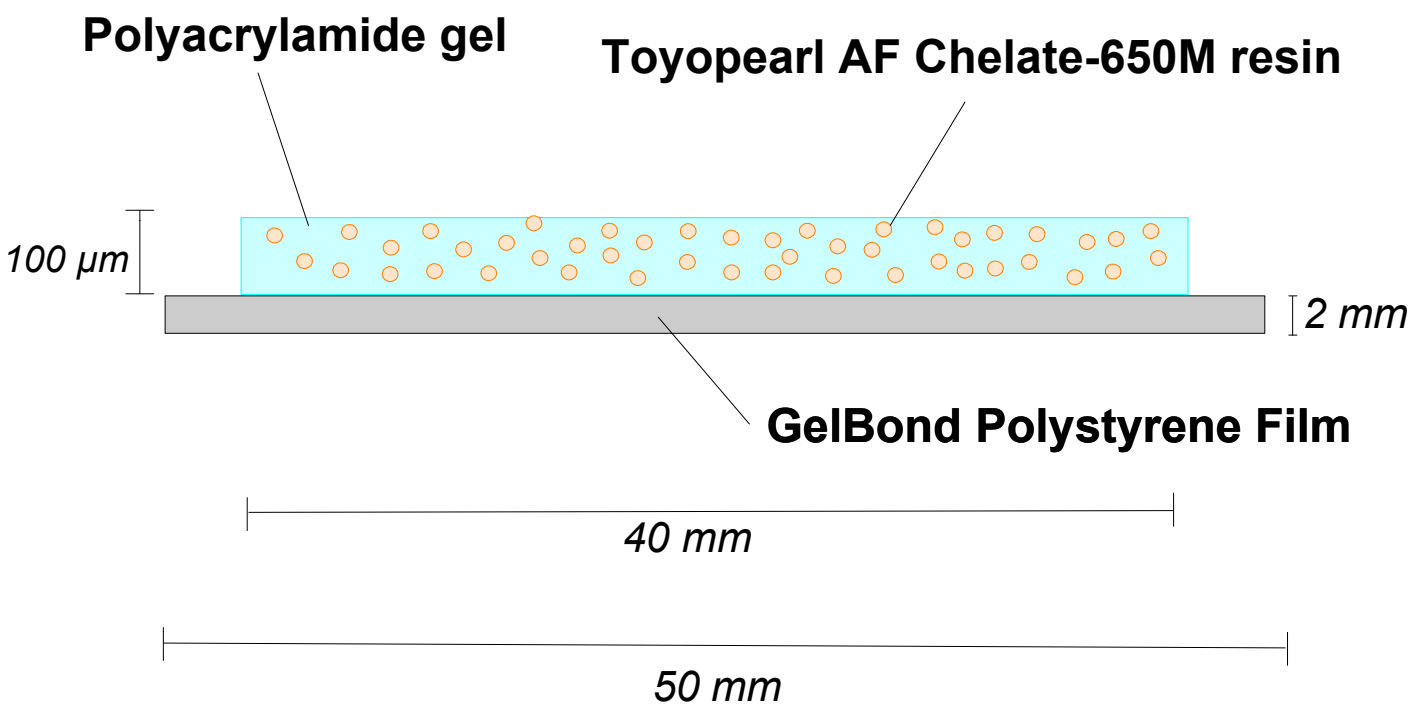
Biotic Ligand Model



Different ions compete for binding sites in a metal mixture



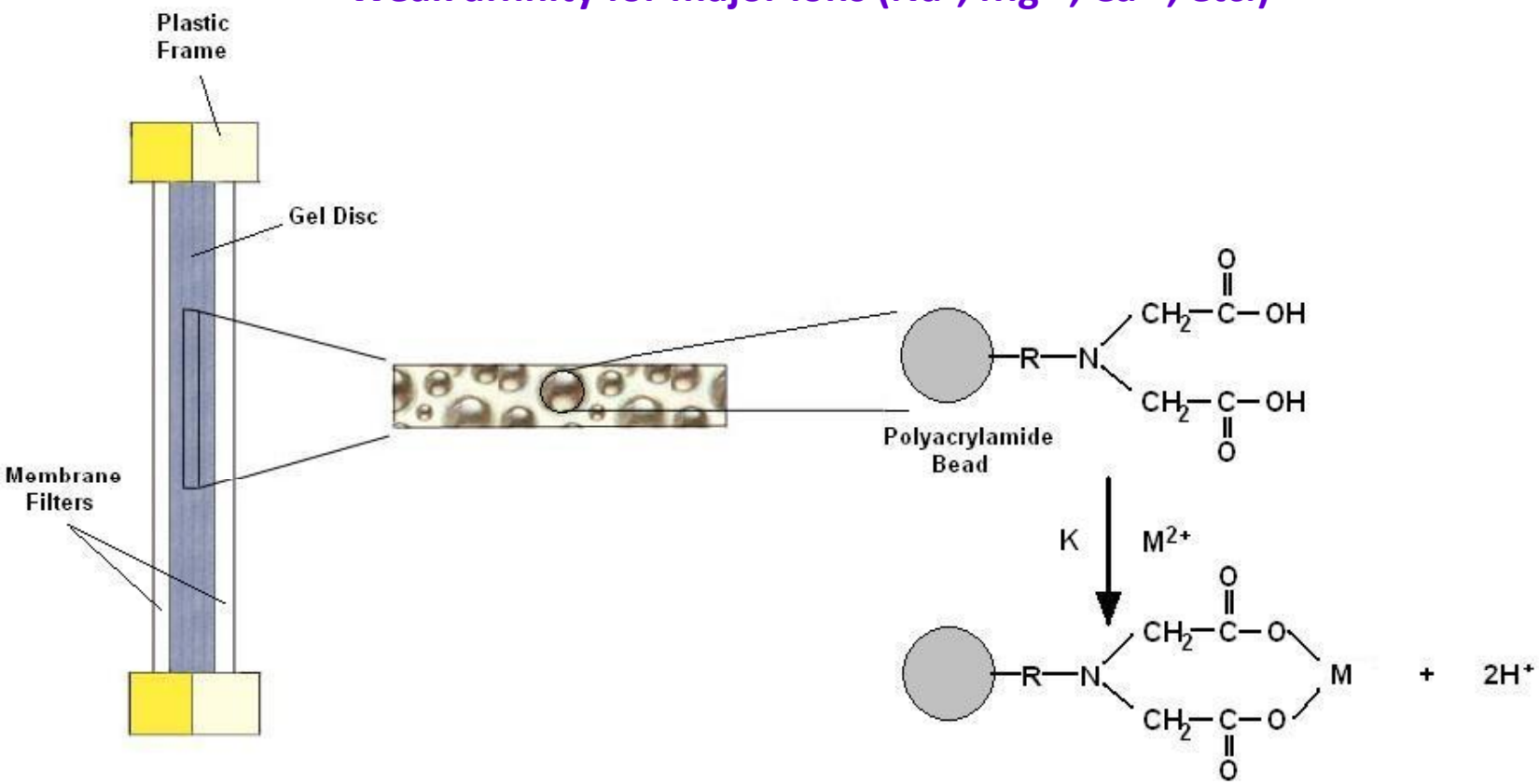
Equilibrium Sampler (Gellyfish) : Design Criteria

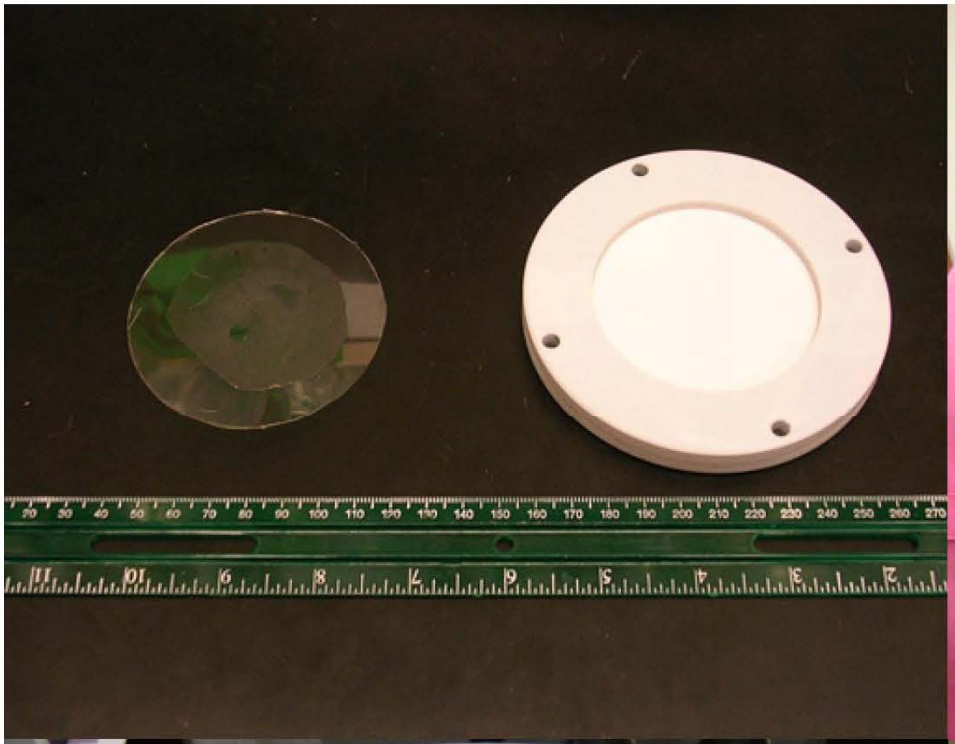


- Metal binding resin held within a polyacrylamide wafer
    - binding sites: Iminodiacetate (IDA)
- IDA sites equilibrate with free metal ions in the surrounding solution
    - Metals back extracted into 5% Nitric Acid
    - Metal analysis by ICP-MS
- Knowledge of IDA affinity for metal allows calculation of free metal ion in surrounding solution

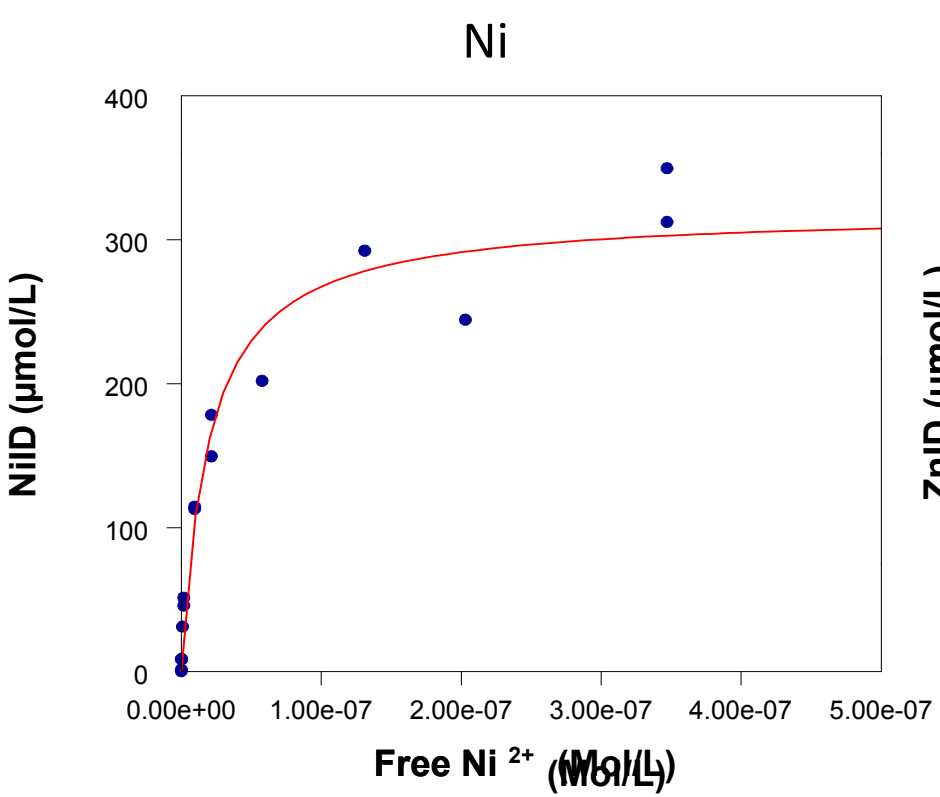
Structure of A Gellyfish Sampler

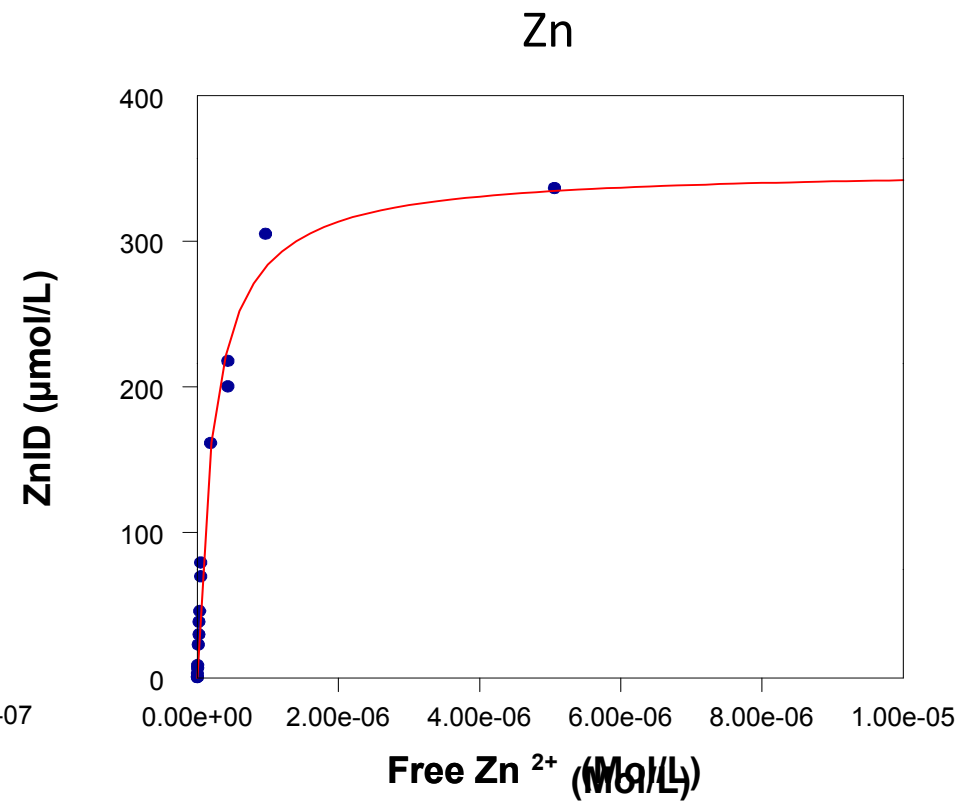
- **Thickness of the gel disc: 100 µm**
- **Diameter of the gel disc: ~ 50 mm**
- **Diameter of beads (Tosoh Bioscience): 65 µm**
- **Weak affinity for major ions (Na^+, Mg^{2+}, Ca^{2+}, etc.)**





Apparent stability constants



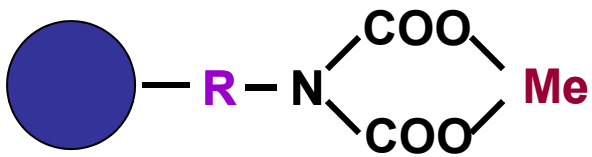


$$[\text{M-Id}] = \frac{[\text{IDA}_{\text{total}}][\text{M}^{2+}]}{\dfrac{1+\sum \text{K}_{\text{i}}[\text{M}_{\text{i}}]}{\text{K}_{\text{M-IDA}}} + [\text{M}^{2+}]}$$

Apparent Stability Constants

* K values of IDA from Martel & Smith, 1974

Species	log K	log K'	95% Confidence Interval
Cu-Id	10.57	10.94	(10.64,13.31)
Zn-Id	7.24	8.71	(8.58,8.87)
Pb-Id	7.45	7.88	(7.85,7.91)
Ni-Id	8.13	9.71	(9.56,9.96)
Cd-Id	5.73	7.96	(7.92, 8.00)



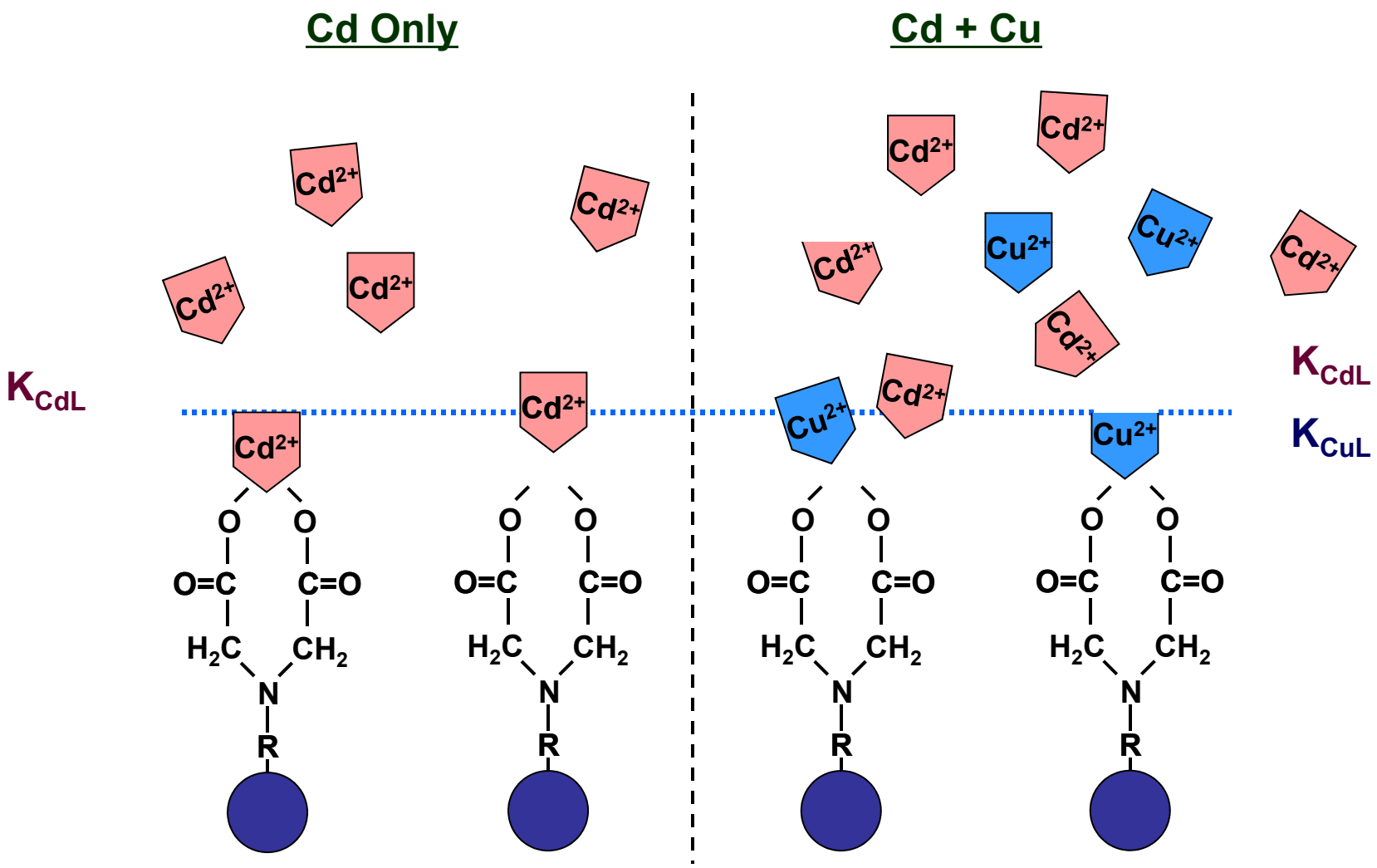
*Limit of Detection (pH=7.8):

Cu: 3.9×10^{-13} M Zn: 2.9×10^{-9} M

Pb: 1.5×10^{-11} M Ni: 2.0×10^{-10} M

Cd: 2.0×10^{-12} M

Accounting for metal-metal competition within the Gellyfish



The GELLYMOD (Module A)

Microsoft Excel - GELLYMOD.xls

D35 =E24/$K43/$K$22

Gellyfish Multiple Metal Model: Model I - Determination of Me^{2+} In the Surrounding Solution Given Measured Amounts of MeIDA Inside the Gellyfish

Model Input:

Gellyfish Characteristics:

Volume	0.375	ml
Bead Slurry	1.50E-02	ml/Gellyfish
IE Capacity	28	uEq/ml

Water Characteristics:

Salinity	23.9	psu
pH	7.66	

Concentration of IDA bound metal within Gellyfish:

Metal	Me-IDA (moles/L)
Cu	1.07E-05
Zn	2.39E-04
Pb	1.75E-08
Ni	4.32E-06
Cd	4.18E-08

Model Output:

Metal	Free Me^{2+} (mol/L)
Cu	4.80E-10
Zn	1.83E-06
Pb	9.04E-10
Ni	3.30E-09
Cd	1.71E-09

Calculated Parameters:

[Mg2+]	0.03622045	mol/L
[Na+]	0.3183958	mol/L
[Ca2+]	0.00696685	mol/L
[H+]	2.19E-08	mol/L
[Sr2+]	0	mol/L
[Cl-]	0.3712148	mol/L
[SO42-]	0.01910805	mol/L
[HCO3-]	0.0015774	mol/L
[BO33-]	0.000321694	mol/L
[Br-]	0.000557229	mol/L
Ionic Strength	4.72E-01	mol/L
Activity Coefficient:	0.94	(monovalent)
(Davies Equation)	0.77	(bivalent)
[IDA]-Total	2.80E-04	eq/L
[IDA]-free	4.29E-07	eq/L
[MgID]	8.83E-06	mol/L
[NaID]	2.41E-07	mol/L
[CaID]	6.92E-07	mol/L
[HID]	1.58E-05	mol/L
[H_2ID]	1.24E-10	mol/L
[SrID]	0.00E+00	mol/L

Condtional Stability Constants:

Species	K
Mg-IDA	5.69E+02
Na-IDA	1.77E+00
Ca-IDA	2.32E+02
H-IDA	1.69E+09
H2-IDA	6.04E+11
Cu-IDA	5.19E+10
Zn-IDA	3.05E+08
Pb-IDA	4.52E+07
Ni-IDA	3.05E+09
Cd-IDA	5.69E+07
Sr-IDA	1.01E+02

Thermodynamic Database:

Species	Log K	I
Mg-IDA	2.98	0.1
Na-IDA	0.36	0.1
Ca-IDA	2.59	0.1
H-IDA	9.34	0.1
H2-IDA	11.95	0.1
Cu-IDA	10.94	0.1
Zn-IDA	8.71	0.1
Pb-IDA	7.88	0.1
Ni-IDA	9.71	0.1
Cd-IDA	7.98	0.1
Sr-IDA	2.23	0.1

Model I - MeID Known, Me2+ Unkn | Model I Description | Model II-Me2+ Known, MeID Unkn | Model II De

Ready Sum=1.83E-06 NUM

start | GELLYMOD | Appendix.doc - Mi... | Microsoft PowerP... | Microsoft Excel - ... | 1:43 AM

The GELLYMOD (Module B)

Microsoft Excel - GELLYMOD.xls

yfish Multiple Metal Model: Model II - Determination of MeIDA Inside Gellyfish Given a Known Amount of Me^{2+} in Surrounding Solution

Global Model Model Inputs:

Gellyfish Characteristics:

Volume	0.375	ml
Bead Slurry	1.50E-02	ml/Gellyfish
IE Capacity	28	uEq/ml

Water Characteristics:

Salinity	23.9	psu
pH	7.89	

Starting/Finishing Values of Me^{2+}:

	Cu^{2+} (Mol/L)	Zn^{2+} (Mol/L)	Pb^{2+} (Mol/L)	Ni^{2+} (Mol/L)	Cd^{2+} (Mol/L)
Start (Trial 1)	1.00E-10	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Finish (Trial 25)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Calculated Parameters:

[Mg2+]	0.03622	mol/L
[Na+]	0.318396	mol/L
[Ca2+]	0.006967	mol/L
[H+]	1.29E-08	mol/L
[Sr2+]	0	mol/L
[Cl-]	0.371215	mol/L
[SO42-]	0.019108	mol/L
[HCO3-]	0.001577	mol/L
[BO33-]	0.000322	mol/L
[Br-]	0.000557	mol/L
Ionic Strength	4.72E-01	mol/L
Activity Coefficient:	0.94	(monovalent)
(Davies Equation)	0.77	(bivalent)
[IDA]-Total	2.80E-04	mol/L

Condtional Stability Constants:

Species	K
Mg-IDA	5.69E+02
Na-IDA	1.77E+00
Ca-IDA	2.32E+02
H-IDA	1.69E+09
H2-IDA	6.04E+11
Cu-IDA	5.19E+10
Zn-IDA	3.05E+08
Pb-IDA	4.52E+07
Ni-IDA	3.05E+09
Cd-IDA	5.69E+07
Sr-IDA	1.01E+02

Thermodynamic Database

Species	Log K
Mg-IDA	2.98
Na-IDA	0.36
Ca-IDA	2.59
H-IDA	9.34
H2-IDA	11.95
Cu-IDA	10.94
Zn-IDA	8.71
Pb-IDA	7.88
Ni-IDA	9.71
Cd-IDA	7.98
Sr-IDA	2.23

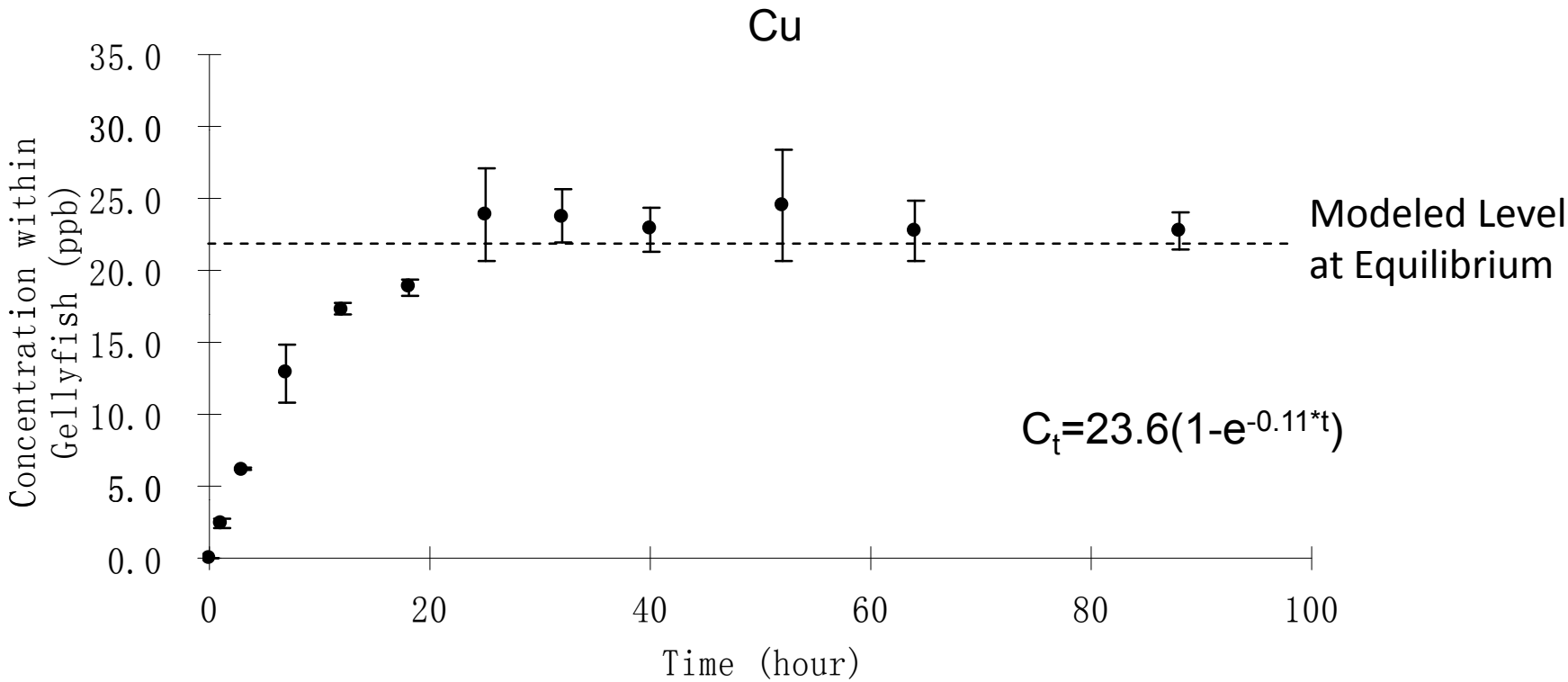
Model Output:

Trial #	$[Cu^{2+}]$ (Mol/L)	$[Zn^{2+}]$ (Mol/L)	$[Pb^{2+}]$ (Mol/L)	$[Ni^{2+}]$ (Mol/L)	$[Cd^{2+}]$ (Mol/L)	[IDfree] (eq/L)	[MgID] (Mol/L)	[NaID] (Mol/L)	[CaID] (Mol/L)	[HID] (Mol/L)	[H2ID] (Mol/L)	[SrID] (Mol/L)	[CuID] (Mol/L)	[ZnID] (Mol/L)	[PbID] (Mol/L)	[NiID] (Mol/L)
1	1.00E-10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.52E-06	1.14E-04	3.11E-06	8.91E-06	1.20E-04	5.54E-10	0.00E+00	2.86E-05	0.00E+00	0.00E+00	0.00E+00
2	9.58E-11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.55E-06	1.14E-04	3.12E-06	8.95E-06	1.21E-04	5.56E-10	0.00E+00	2.76E-05	0.00E+00	0.00E+00	0.00E+00
3	9.17E-11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.57E-06	1.15E-04	3.13E-06	8.99E-06	1.21E-04	5.58E-10	0.00E+00	2.65E-05	0.00E+00	0.00E+00	0.00E+00

Model I - MeID Known, Me2+ Unkn | Model I Description | Model II-Me2+ Known, MeID Unkn | Model II Descrip

Ready

Equilibration Time: hours to a day

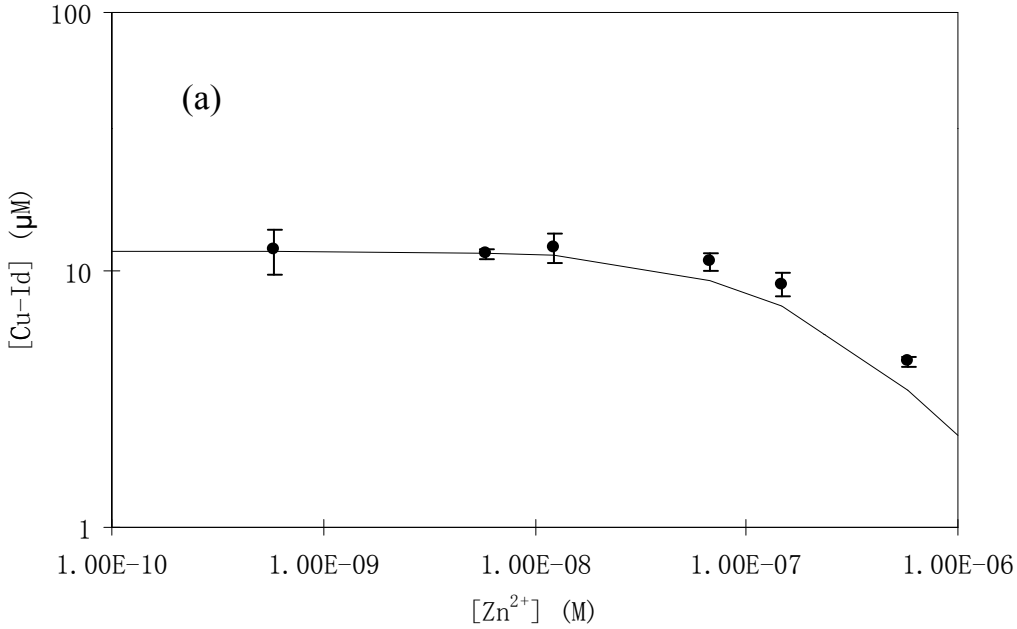


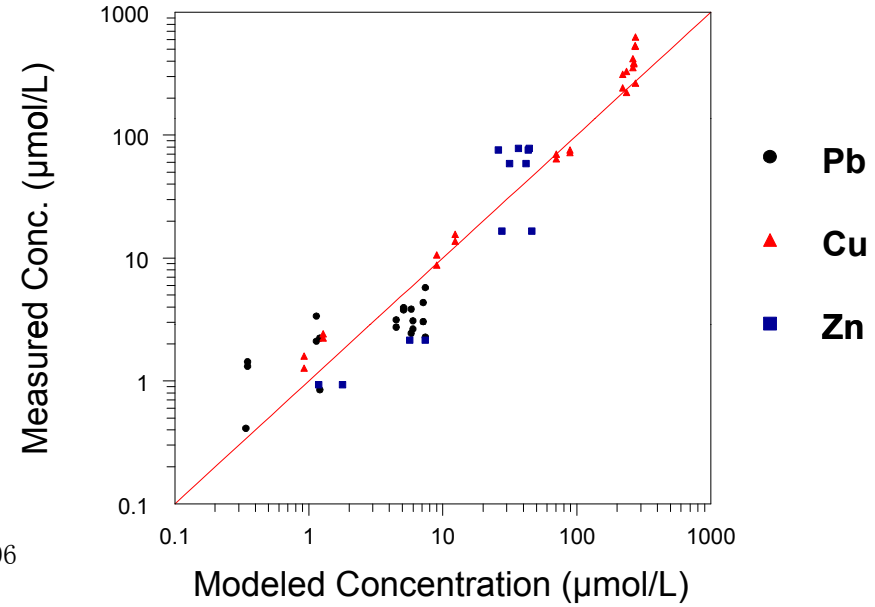
Time to reach 90% equilibrium:

Cu: 22 hours
Zn: 3 hours
Pb: 3 hours
Ni: 62 hours
Cd: 18 hours

Laboratory Validation:
Multiple Metal Competition Experiments

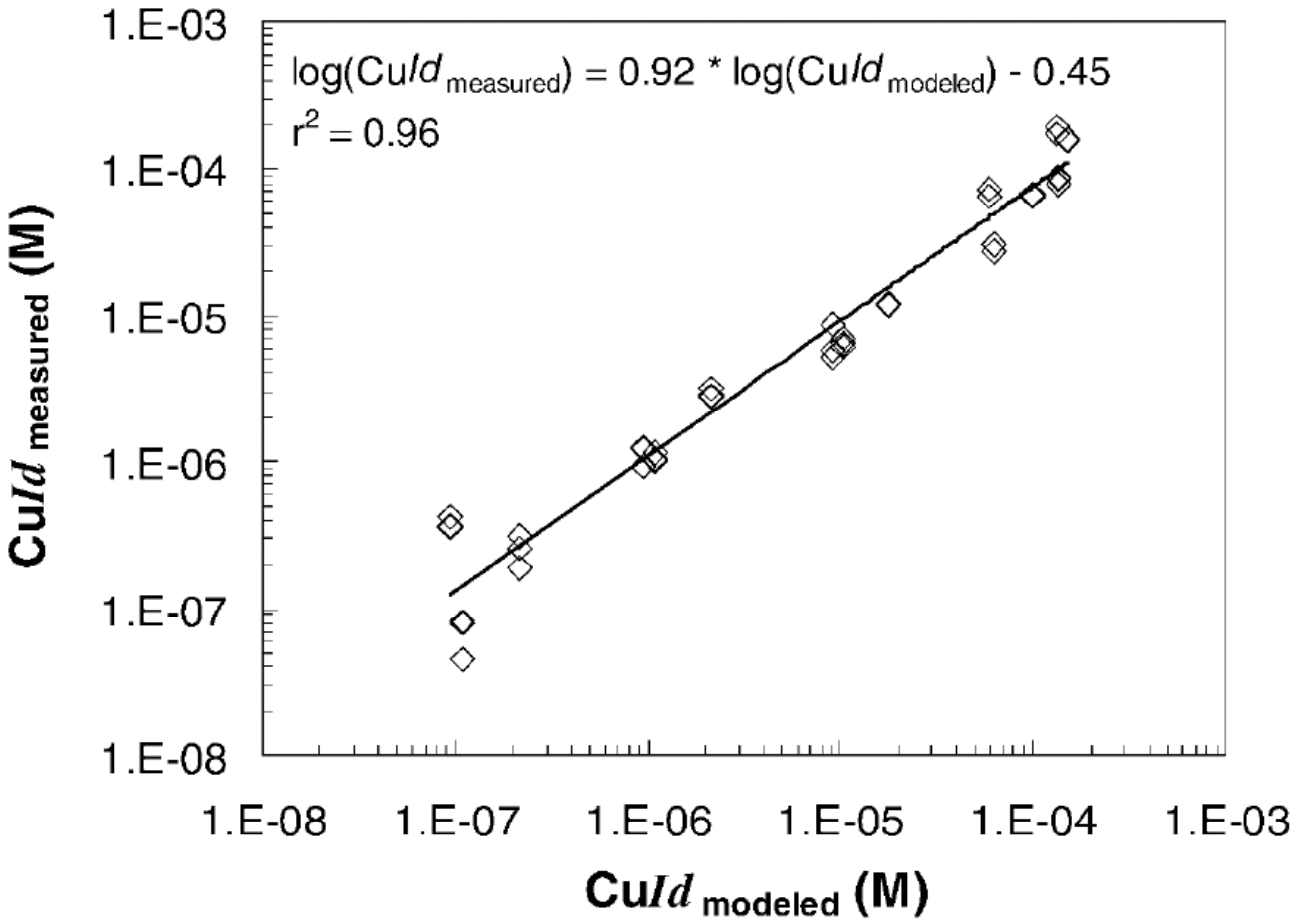
Zn-Cu Competition



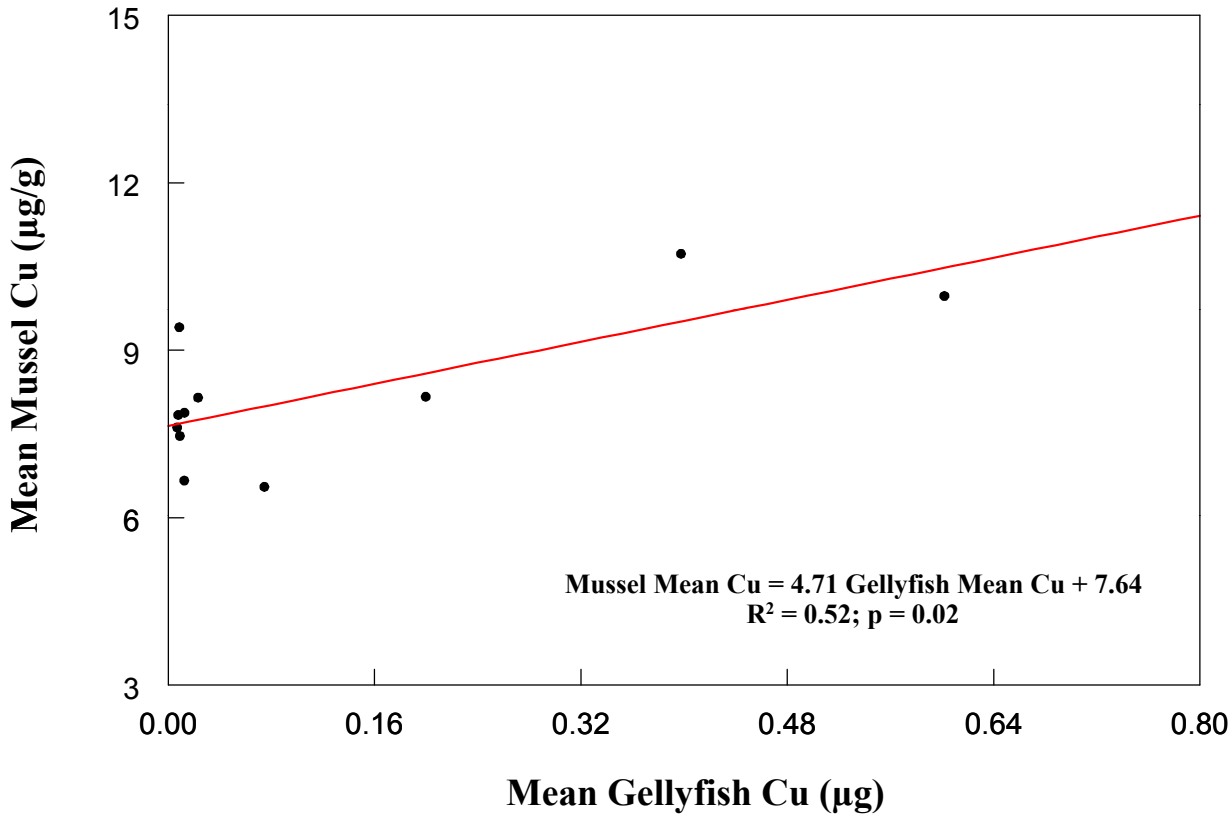


Gellyfish is inert to salinity change.

Salinity Range: 5 – 35 $^{o}/_{oo}$



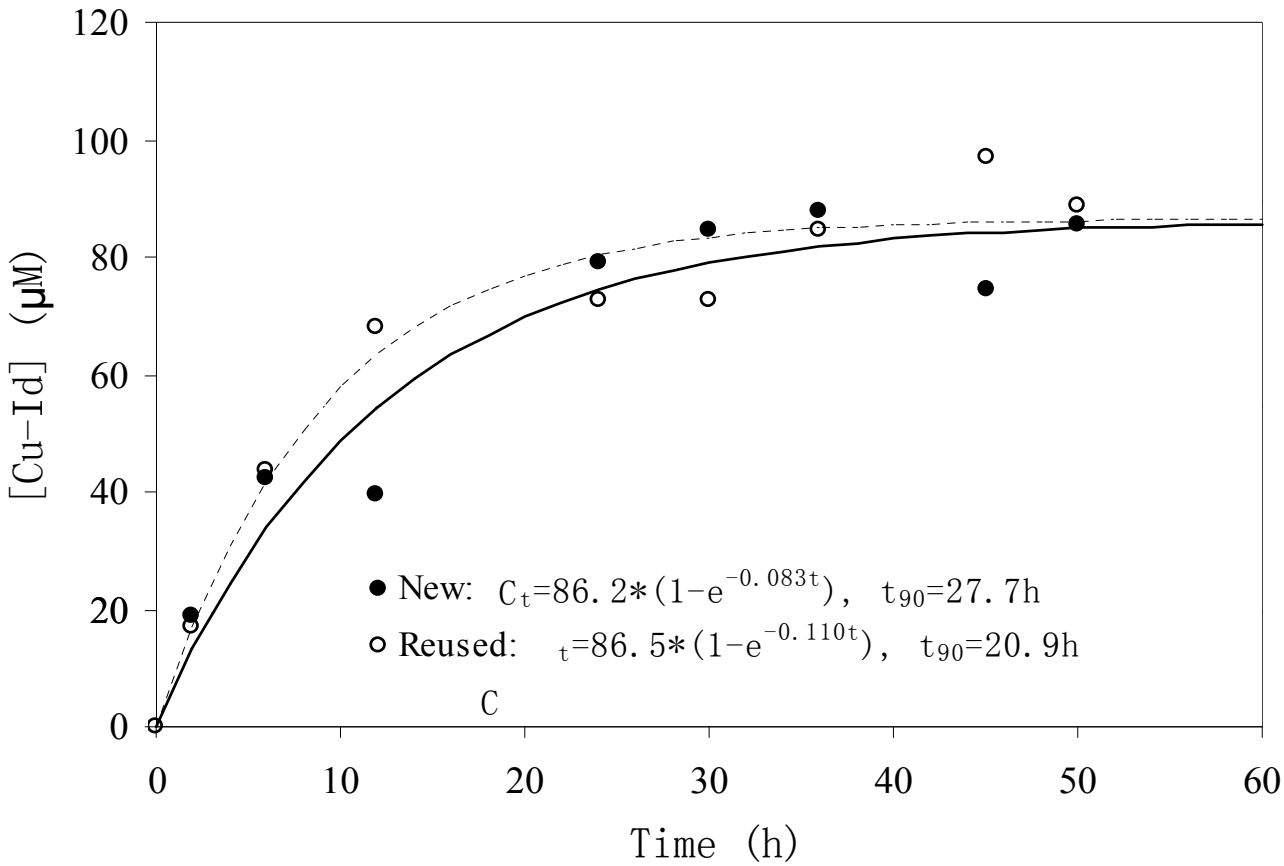
Gellyfish measurements are correlated with metal uptake into marine bivalves.



Compared with mussels, Gellyfish is:

- cheaper: at least 10 times lower in cost
- faster: days vs. months
- less labor-intensive

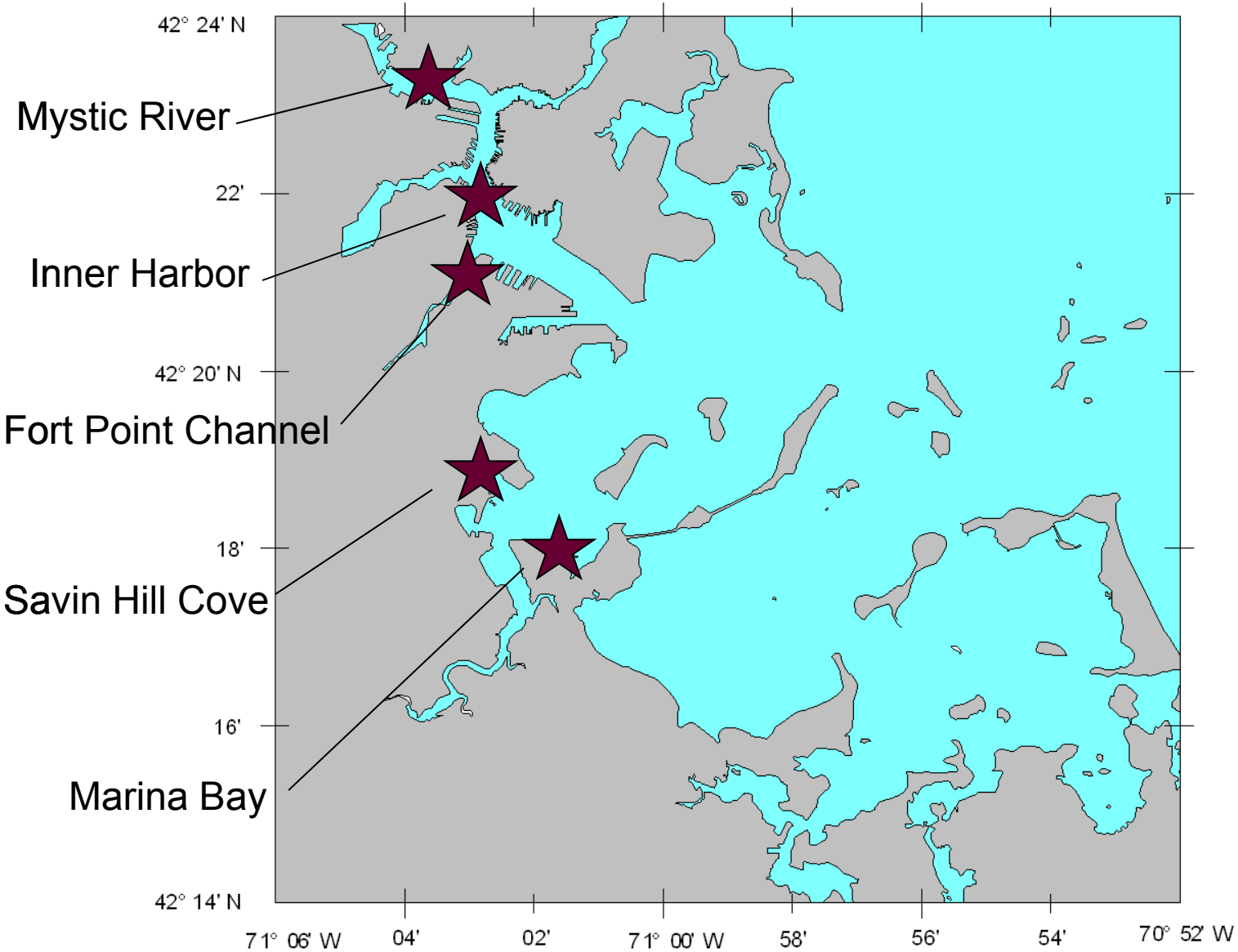
Gellyfish samplers are reusable.



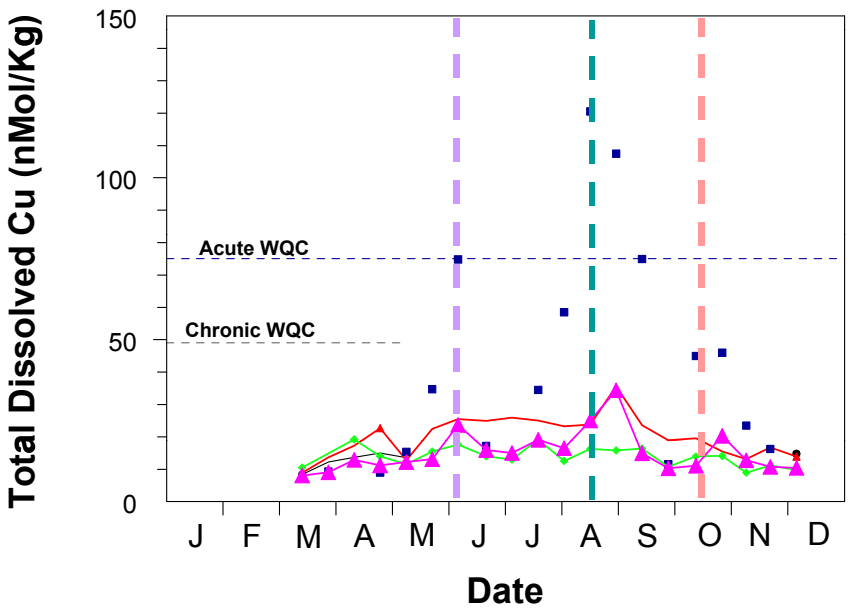
Material cost per each assembled sampler ~ $8:

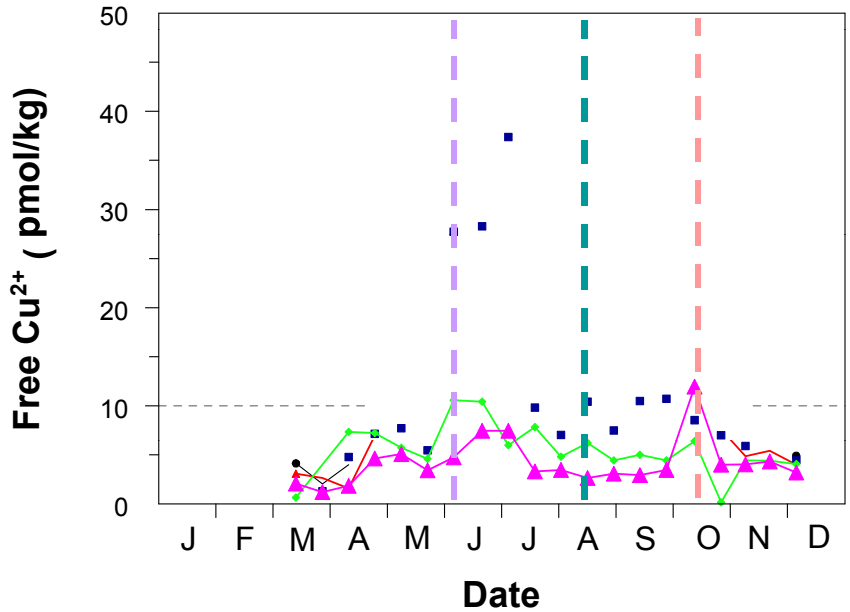
- 2 x Gelbond films: $1 each
- 2 x Supor polysulfone membrane filters: $2 each
- Gel matrix & beads: about $2

Sampling Locations:



Dissolved and Free Cu at All Locations





Fort Pt Channel

Inner Harbor

Marina Bay

Mystic River

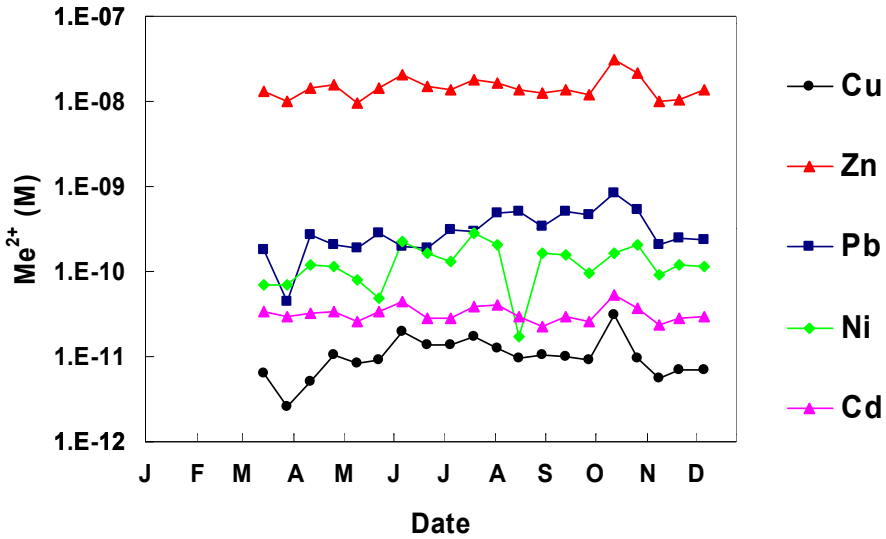
Savin Hill

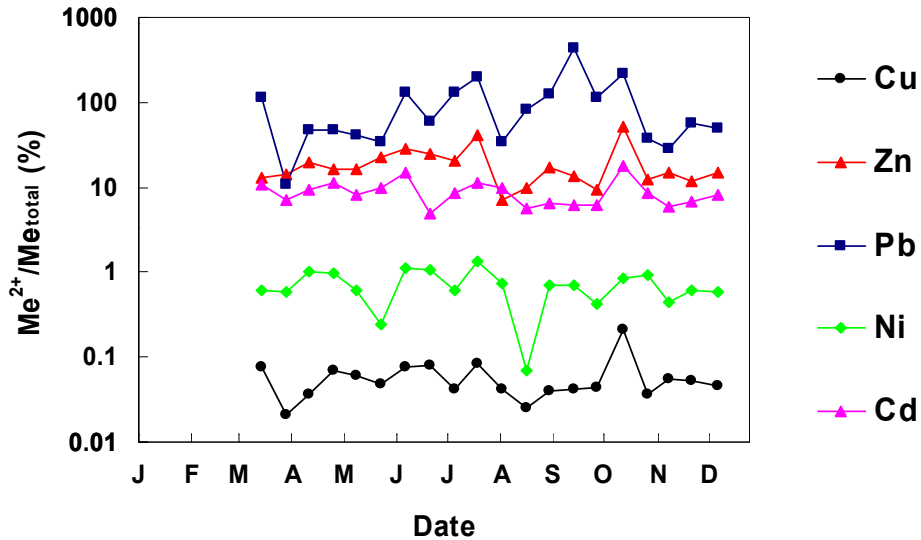
Total vs. Free metal concentrations:

- **One vs. multiple exceedances**
- **Both increase significantly over summer months (inverse U-shape)**
- **Timing of peaks**

Data for All Metals

Location: Fort Point Channel



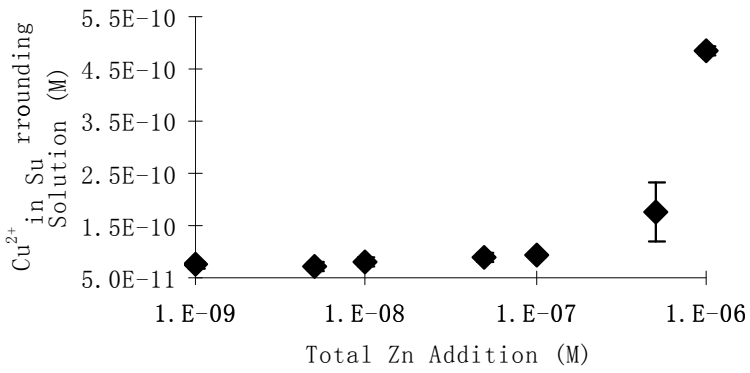


Key Questions:

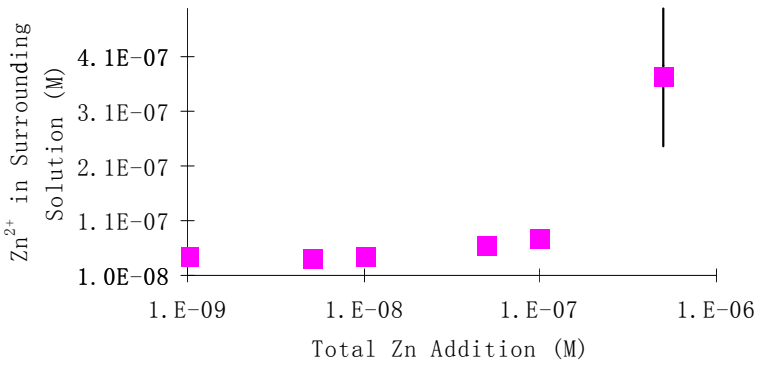
- **Correlations between metals**
- **Relative importance of space vs. time**
- **Similar effect of environmental factors on speciation**

Natural Organic Ligands: NOT metal-specific.

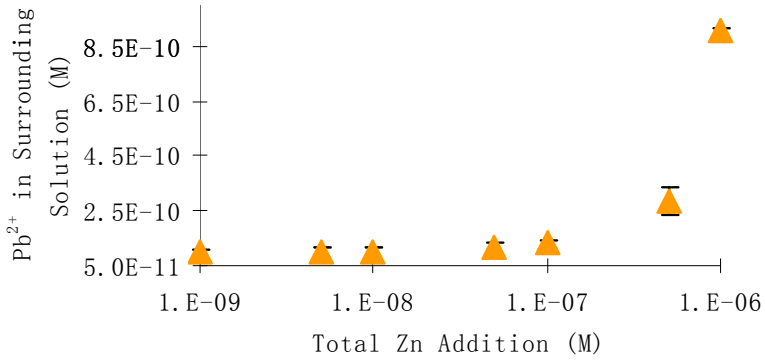
(a) Cu



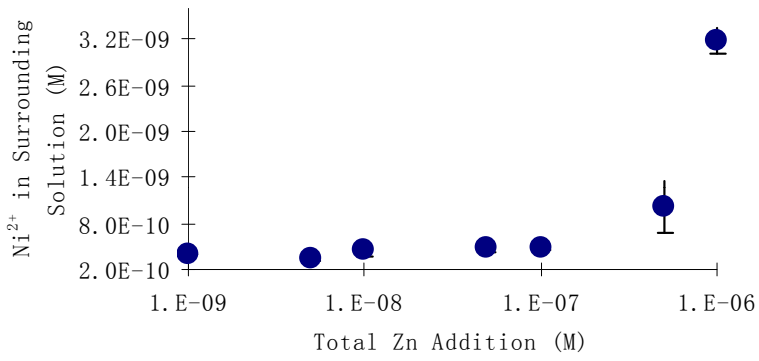
(b) Zn



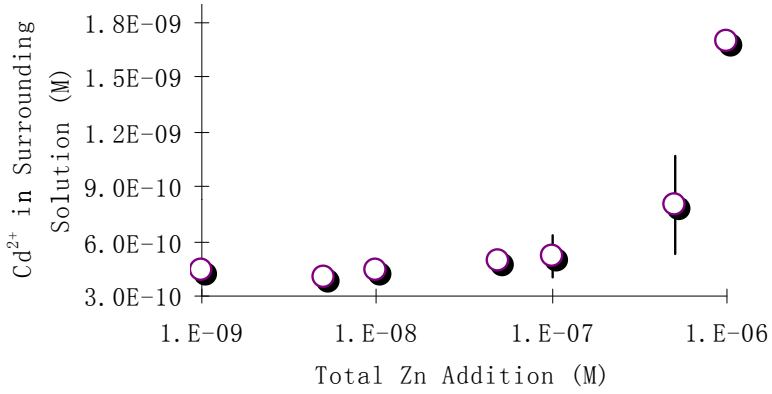
(c) Pb



(d) Ni



(e) Cd



Future Research

- Parallel comparison with other free metal ion determination techniques (e.g. voltammetry, DGT)
- Application to sediment pore water
- Temperature and pH effects

Summary

- Gellyfish is an effective tool for determining free ion concentrations in aquatic environment.
  - Can measure multiple metals
  - Rapid & in-situ
  - Reusable & low cost
  - Easy to make and use
  - Can generate massive datasets
- Can serve as a biomimic in biomonitoring programs.
- Diverse application potentials