Historical Mussel Shells Illuminate Legacy Contaminant Patterns Over the Past 1000 Years

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Trace metals and bivalve shells

- Introduction to theory
  1. Bivalves secrete shells in annual rings
  2. Trace metals are incorporated into annuli
  3. Incorporation is directly correlated to exposure
     - Predict incorporation by 2+ ions
  4. Therefore, shells can be used as archives of past trace metal concentrations
     - Intra-annual analysis
     - Whole-shell analysis

Do shell concentrations vary with shell allometry?

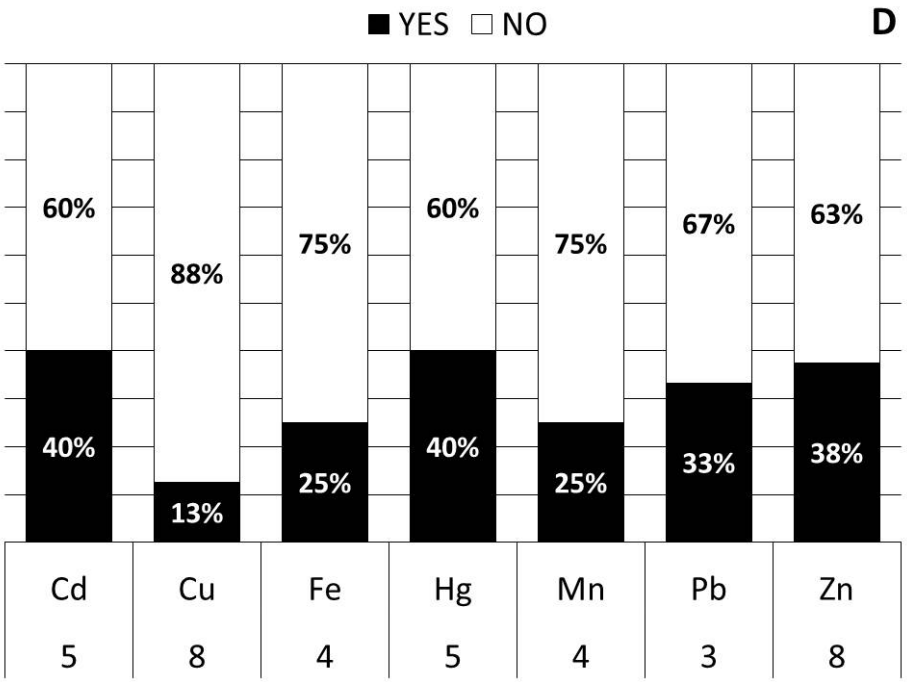


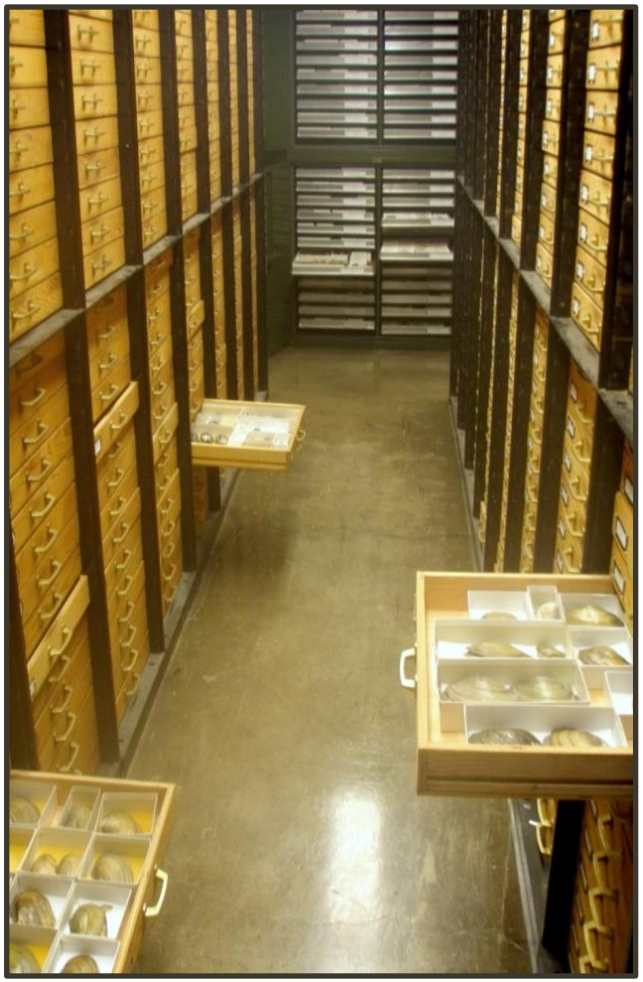
Figure 1 *From Shoults-Wilson (*In sub*). Meta-analysis of literature analyses of trace metal concentrations in whole shells. The question asked of each paper with whether shell concentration directly correlates with shell length.*

- Shell size
  - Length, height, width
- Shell age
- Indices
  - Shell thickness
  - Average growth rate
- Shell length is the only parameter previously studied

Objectives

1. Assess usefulness of bivalve shells as pollution archives
   - Can elements of concern be detected?
   - Is allometry confounding?
2. Create a spatial-temporal map of trace element contamination
   - Time or spatial gradients?

Shells used in the current study: *Amblema plicata* from IL River



INHS mollusk collection

- Field collection
- INHS mollusk collection
  - >430,000 specimens
  - 1861-present
- Archeological specimens (1000 years old)
  - Illinois State Archeological Survey
  - Illinois State Museum

Methods

1. Mussel shells sectioned across all growth lines
2. Shell sections washed
   - Complete digestion of organic matter
   - US EPA protocol
3. Microwave-assisted acid digestion
4. Analysis using ICP-MS

Trace element detection

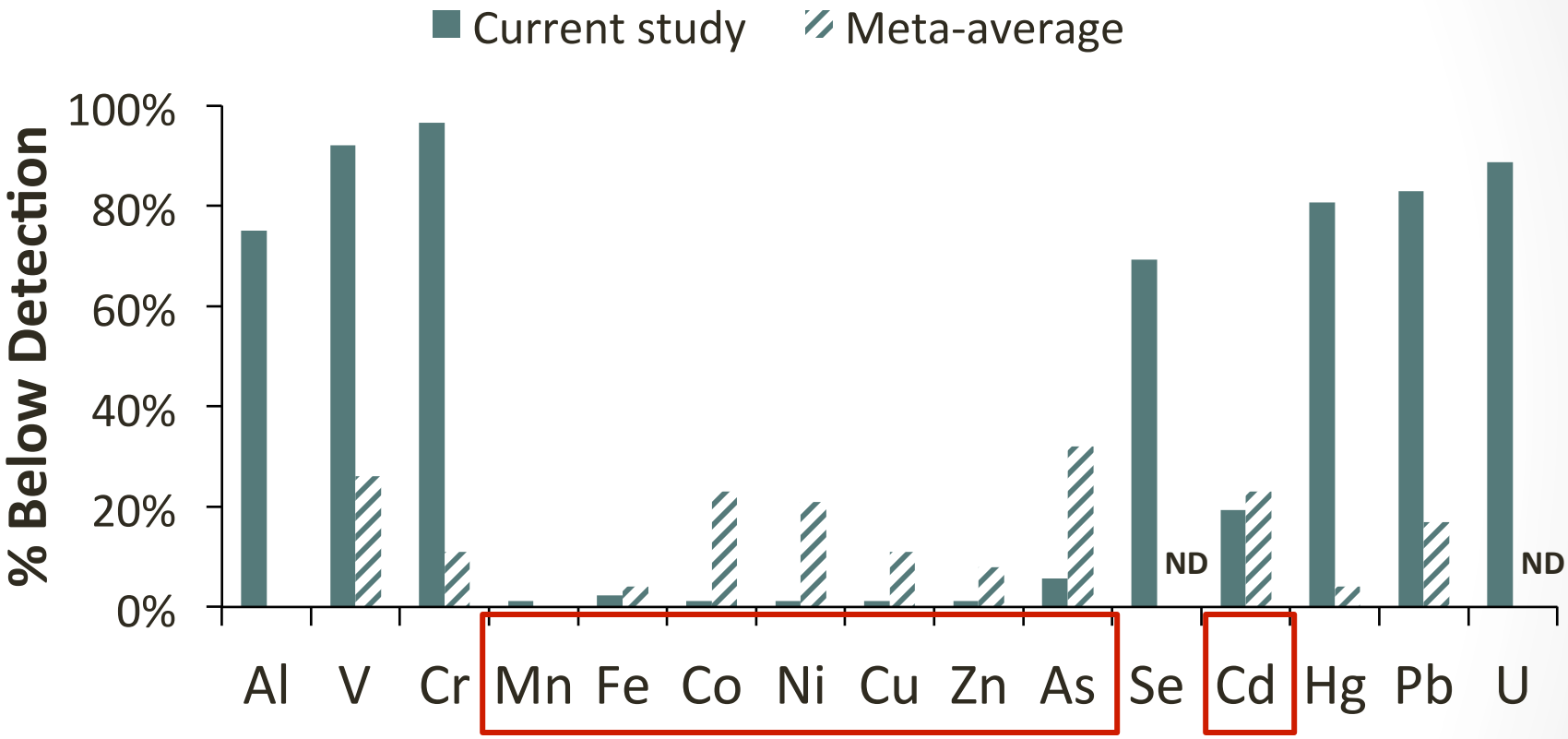


Figure 2 *The percentage of samples that were below detection compared to a meta-analysis of current literature. ND = No Data.*

Archaelogical vs. historic shells

Table 1 *Average concentrations (ppm) of trace elements from* A. plicata *shells samples from near Havana, IL at different times.* ***Bold*** *values are significantly different from archaeological shells. All values are allometry-standardized if applicable.*

Year	Mn	Fe	Co	Ni	Cu	Zn	As	Cd
~1000 AD	555	29.1	1.15	17.0	0.422	3.50	0.054	0.0290
1897	399	**13.2**	1.25	18.5	**1.09**	**2.11**	**0.135**	**0.0164**
1911	374	22.5	1.18	17.8	**0.79**	**1.94**	**0.143**	**0.0148**
1966	289	22.3	1.66	25.5	**1.96**	**2.05**	**0.142**	**0.0199**
2013	315	**15.1**	1.82	25.8	**1.86**	**2.06**	0.084	0.0219

- Cu and As significantly higher compared to prehistoric samples
- Fe, Zn and Cd significantly lower

The significance of allometric relationships

- Relationship with highest significance varied from site to site
- Certain elements more likely to show relationship
- Within a species, relationships consistently in same direction

The significance of allometric relationships

Table 2 *Percentage of allometric variable/element combinations chosen as the strongest relationship.*

Metal (*n*)	Age	Mass	Length	Height	Width	STI	Growth	Overall
Mn (22)	23%	5%	14%	9%	5%		9%	**64%**
Fe (22)			5%	9%		9%	5%	**27%**
Co (22)	14%		9%		5%	5%	9%	**41%**
Ni (22)	5%		14%		5%	5%	14%	**41%**
Cu (22)	5%		9%	9%			5%	**27%**
Zn (22)	5%	5%	5%			9%	5%	**23%**
As (22)	9%		14%			5%	5%	**32%**
Se (8)					13%			**13%**
Cd (22)	9%				9%		5%	**23%**
Overall (184)	**9%**	**1%**	**8%**	**3%**	**3%**	**4%**	**7%**	

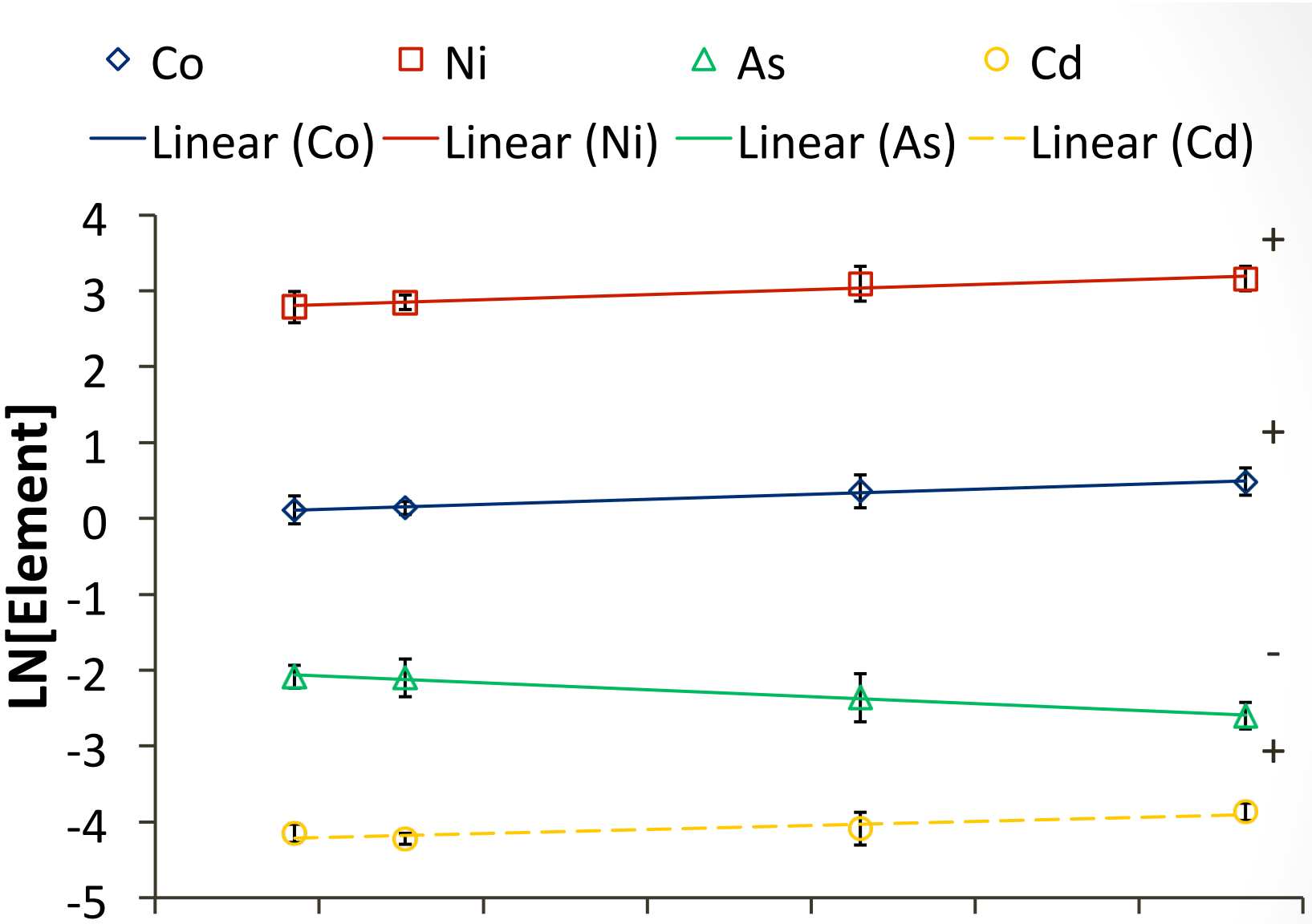


Figure 3 *Significant linear trends between [Element]$_{shell}$ and time of sampling for* A. plicata *shells. Solid lines significant at α = 0.05 and dashed lines significant at α = 0.10.*

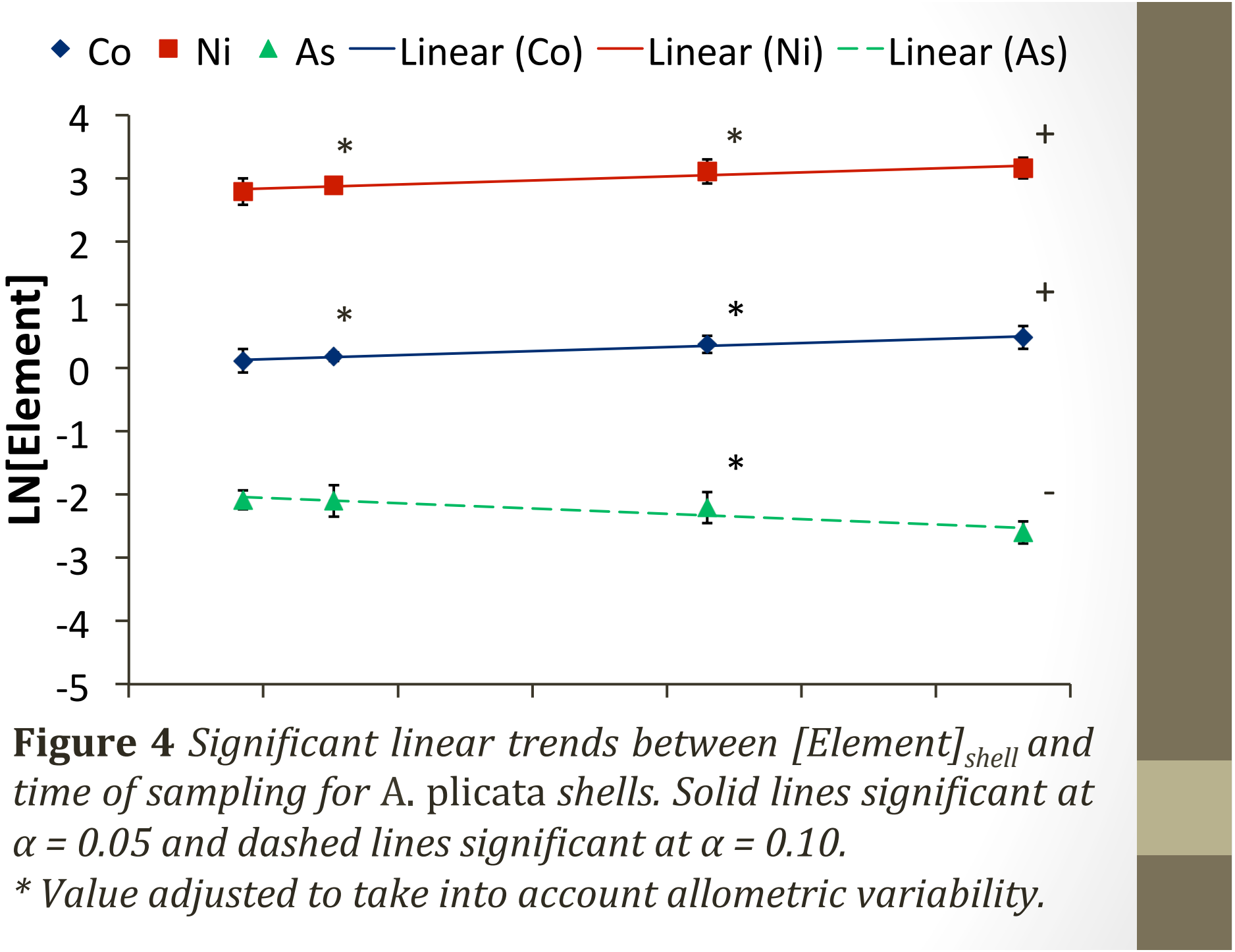


Figure 4 *Significant linear trends between [Element]$_{shell}$ and time of sampling for* A. plicata *shells. Solid lines significant at α = 0.05 and dashed lines significant at α = 0.10.*

** Value adjusted to take into account allometric variability.*

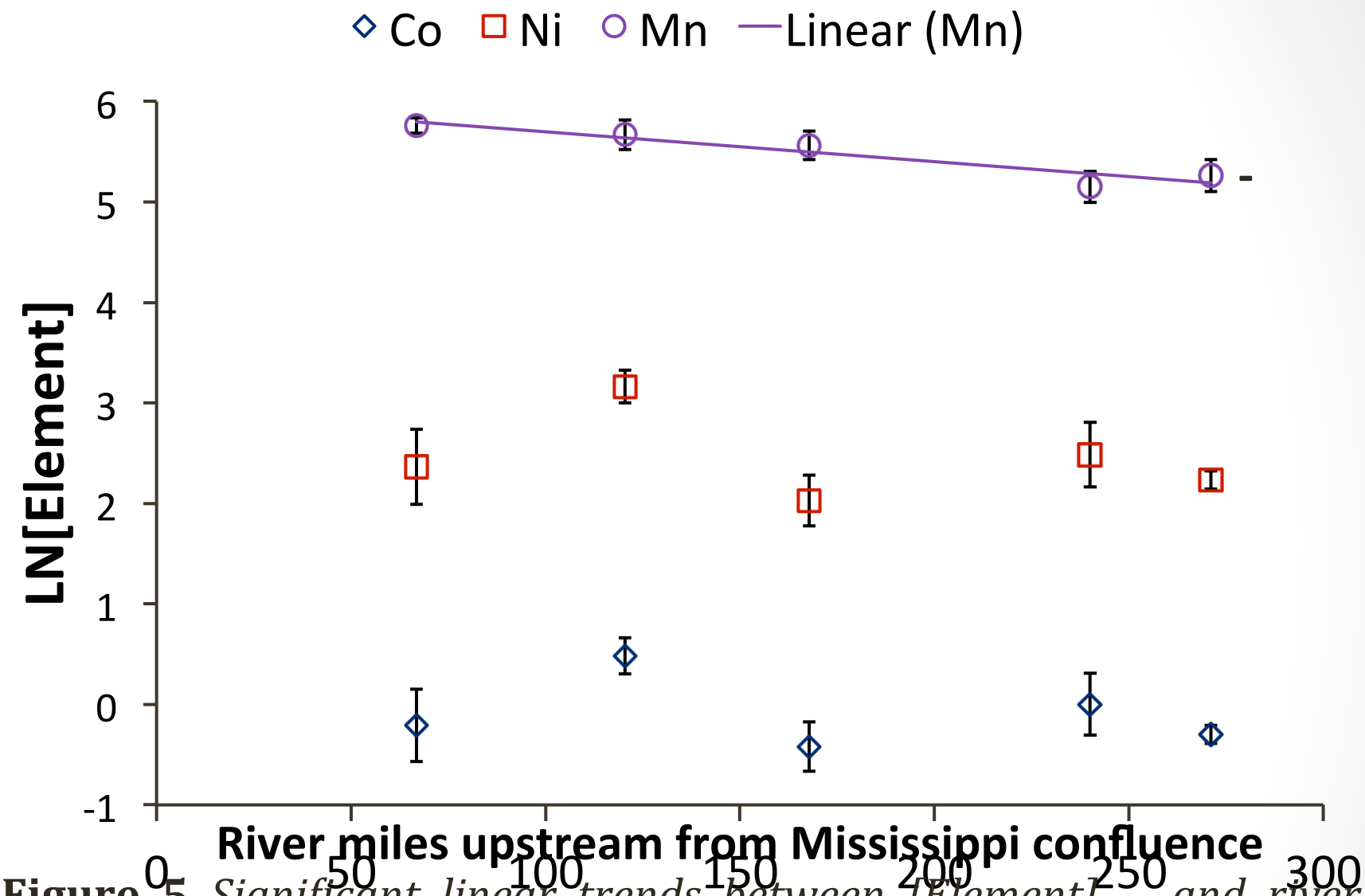


Figure 5 *Significant linear trends between* $[Element]_{shell}$ *and river miles in modern* A. plicata *shells. Solid lines significant at* $\alpha = 0.05$ *and dashed lines significant at* $\alpha = 0.10$.

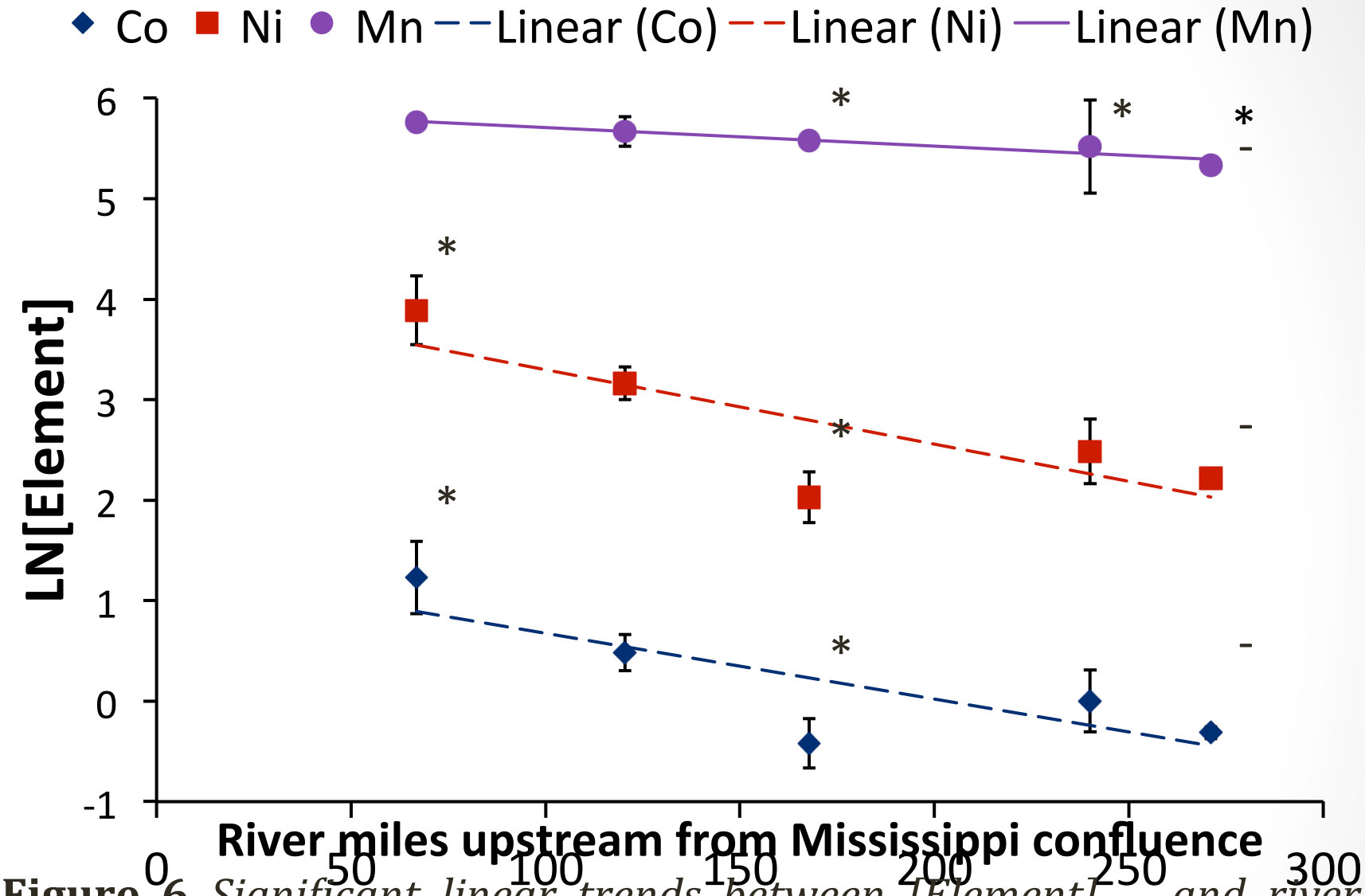


Figure 6 *Significant linear trends between [Element]$_{shell}$ and river miles in modern* A. plicata *shells. Solid lines significant at α = 0.05 and dashed lines significant at α = 0.10.*

** Value adjusted to take into account allometric variability.*

Cross-species comparisons

- *Amblema plicata* vs. *Quadrula quadrula*
  - 5 sites from the Illinois River
  - No element consistently significantly different
- *Actinonaias ligamentina* vs. *Quadrula pustulosa*
  - 1 site from the Kankakee River
  - Cu, Zn, Cd significantly different

Future questions: Do shells reflect environmental concentrations?

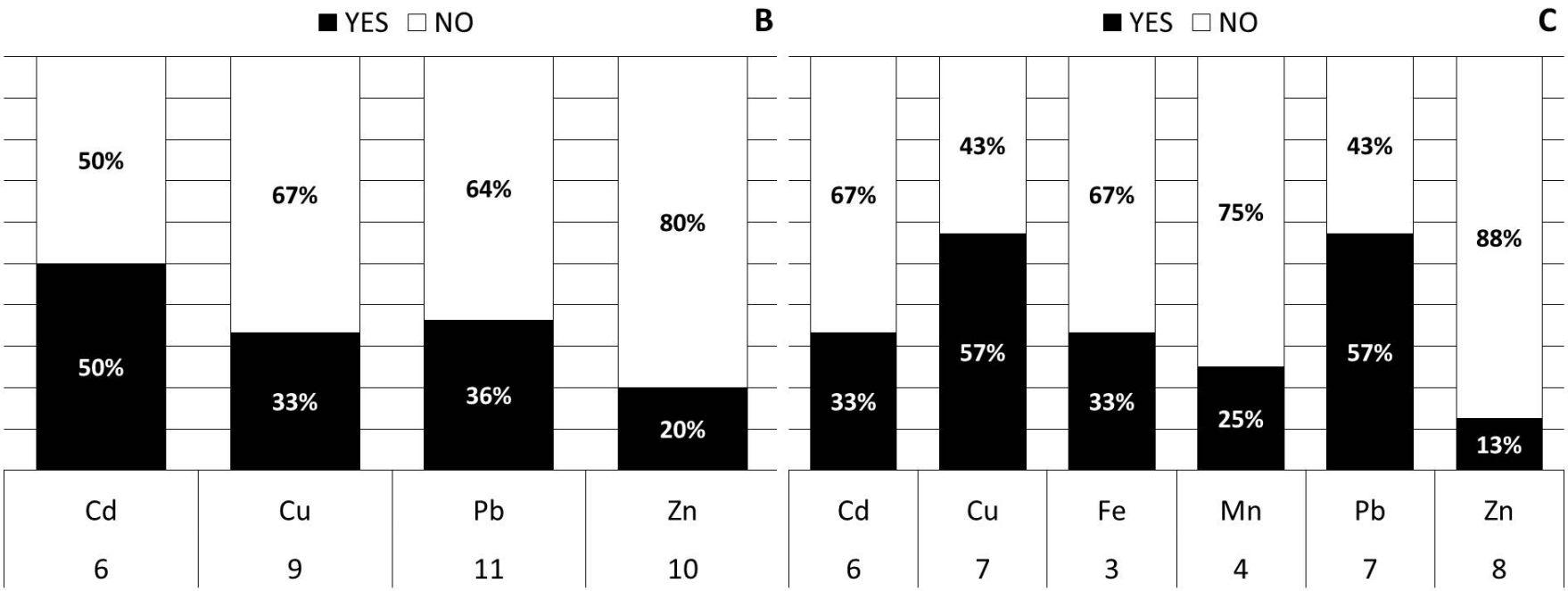


Figure 7 *From Shoults-Wilson (*In sub*). Meta-analysis of literature analyses of trace metal concentrations in whole shells. The question asked of each paper with whether shell concentration directly correlates with metal concentration in sediment (**B**) or water (**C**).*

Other future directions

- Tissue/shell comparison
  - Correlation
  - Limits of detection
  - Within-site variability
  - Seasonality
- Intra-annual analysis of growth rings

Questions?

An example of intra-annual sampling

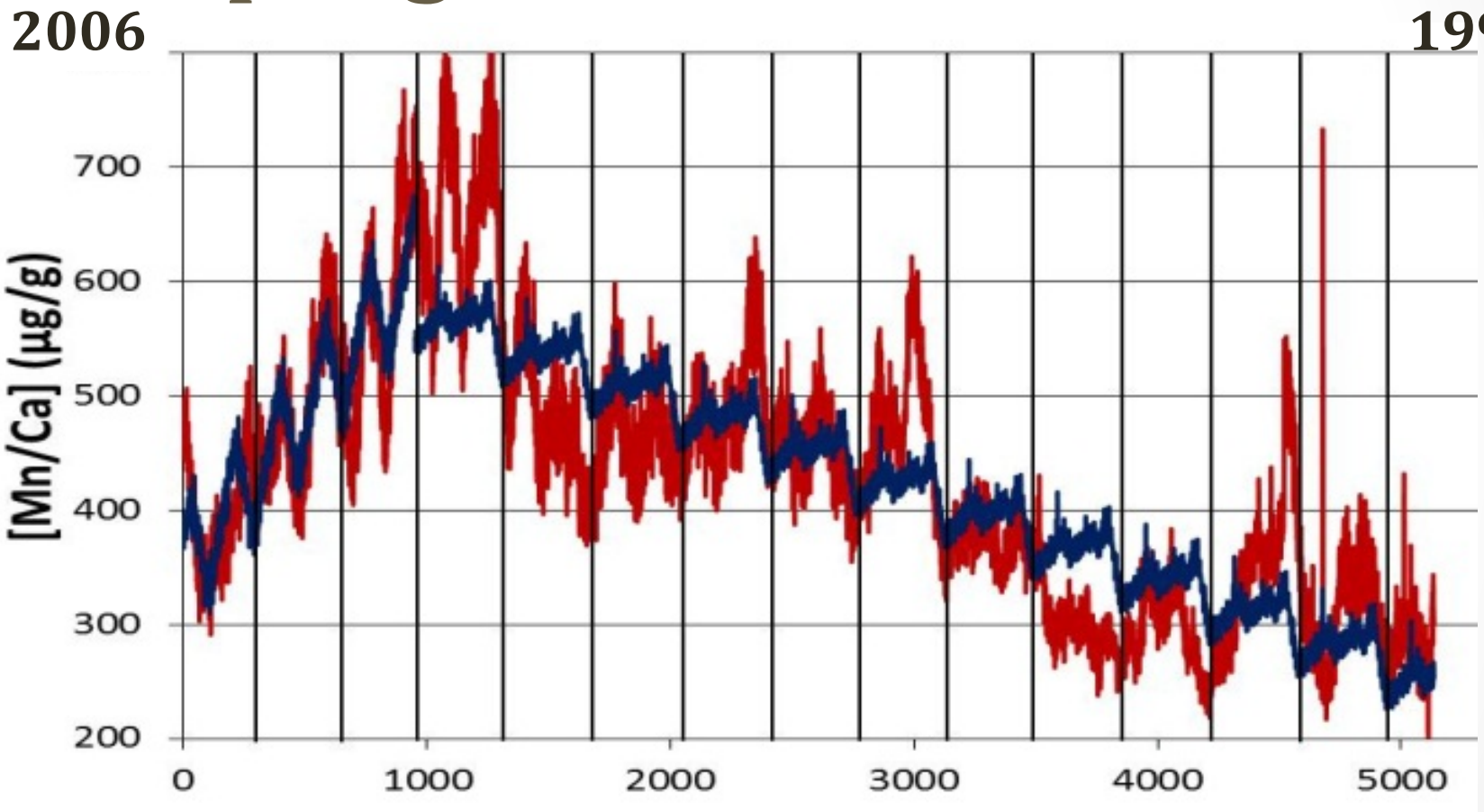


Figure 1. *From Shoults-Wilson et al. 2014. Vertical lines denote annuli as described by [Mn/Ca] data in freshwater mussels (red lines) averaged seasonally (indigo lines). This represents 14 years of accumulation.*

Or going back even further…

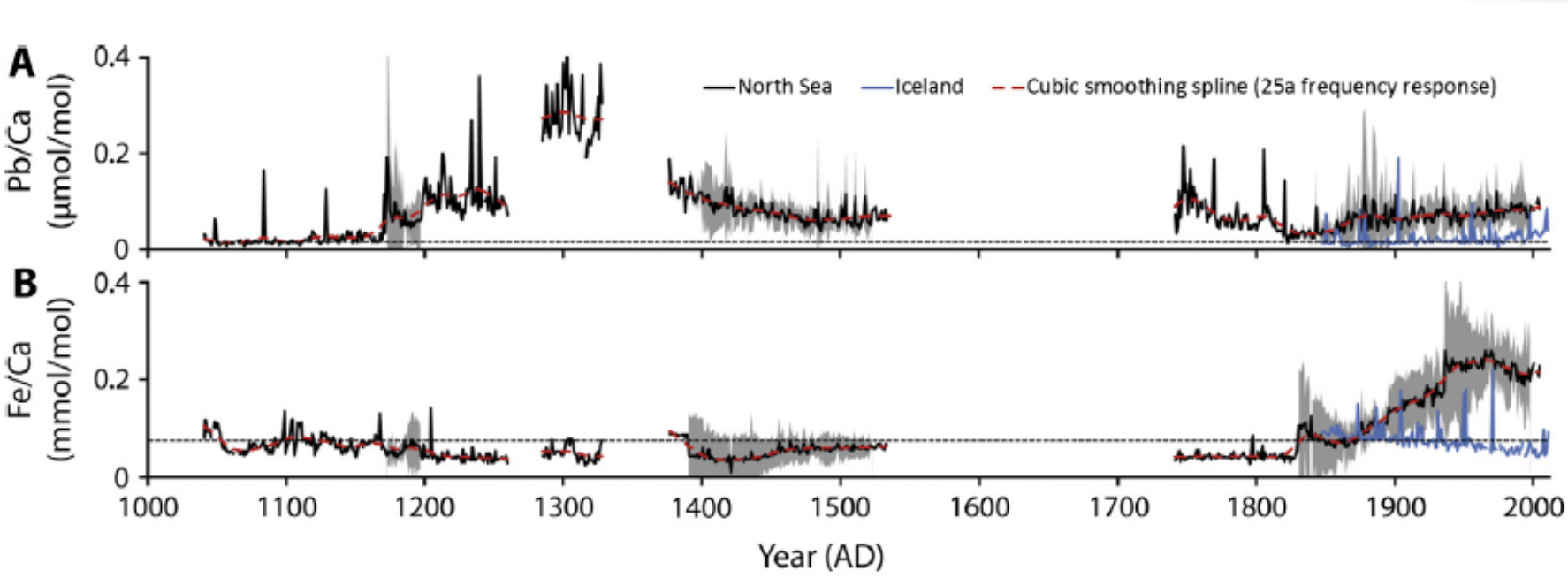


Figure 2 *From Hillard et al. 2014. Annual patterns of Pb and Fe from archaeological* Arctica islandica *shells collected from the North Sea and Iceland. This was used to reconstruct environmental history of the region.*

Conclusions

1. Bivalve shells not suitable for detecting all elements in IL River
   - Important pollutants Pb and Hg not detectable
2. Allometry provides important context
   - Can obscure significant relationships and indicate spurious relationships
3. Elements in IL River have changed over historic period
   - Co & Ni have ↑, while As has ↓
4. Elements in IL River vary spatially