

The Role of Benthic Macrofauna in Influencing Fluxes and Speciation of Dissolved Zinc and Copper in Estuarine Sediments

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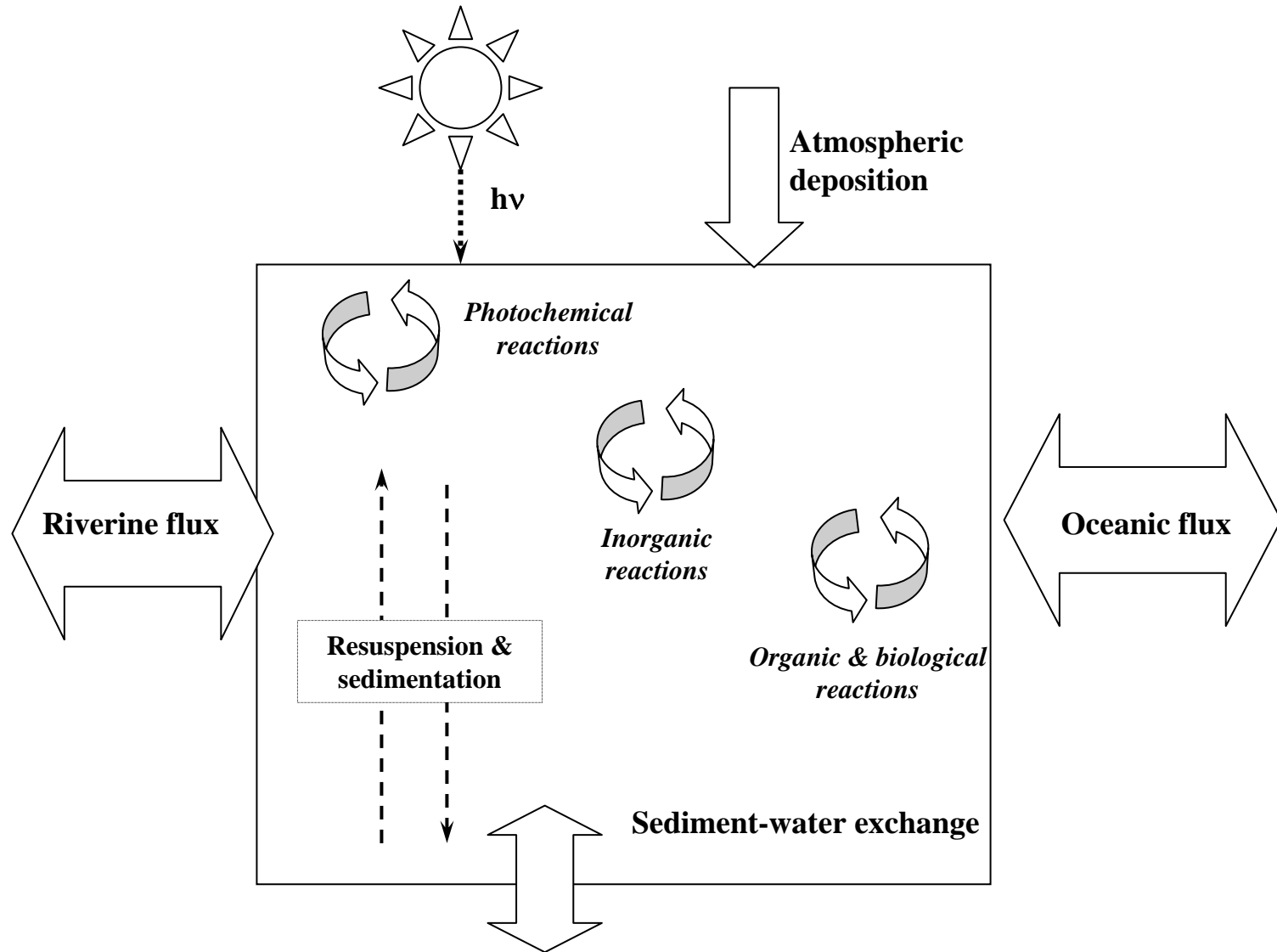
Why Study Copper and Zinc?

- Can be toxic to biota
- Non-toxic at low conc.'s
- Ubiquitous
- Numerous anthropogenic sources
- Toxicity, bioavailability controlled by speciation

Why study the estuary?

- Mixing zone between ocean and river
- Interface between fresh and saline systems
- Unique chemistry

Estuarine Box Model



Speciation of Cu and Zn

- **Cu** in the estuary: >99.9% occurs as Cu-L
- **Zn** in the estuary: 1-95% occurs as Zn-L
- Therefore, characterization of ligands crucial to understanding chemistry of Cu and Zn

Benthic Fluxes

- “Benthic” = bottom of estuary
- Sediments can be important sources or sinks for ligands, metals
- “Flux” = rate at which concentration of substance increases or decreases across sediment-water interface per m^2
- Flux: measured in $\frac{\text{nmol}}{\text{m}^2\text{d}}$

Benthic Fluxes

- **Fluxes** can be diffusive
- **Fluxes** can be mediated by organisms
 - “bioturbation”

Might benthic organisms
influence fluxes in the
CFE?

Streblospio benedicti:

a polychaete that is
common in the CFE

S. benedicti



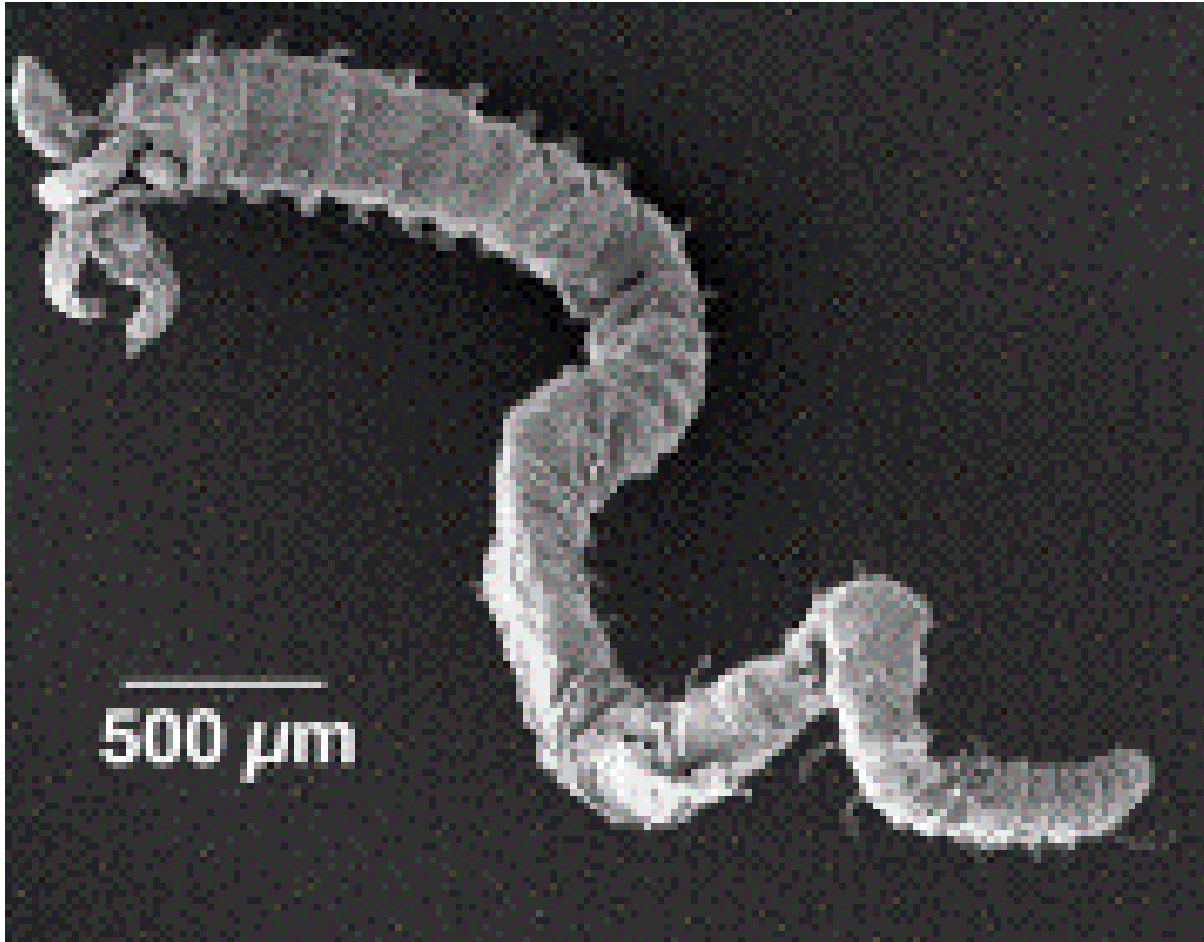
Photo courtesy of Dr. Martin Posey, UNCW-CMS

S. benedicti



Photo courtesy of Dr. Martin Posey, UNCW-CMS

S. benedicti



Source: Salton Sea Benthic Research Group

S. benedicti:

- Burrowing animal
- Can quickly rearrange sediment surfaces
- Hearty, opportunistic organism
- Normal density: 2,000 individuals per m²

Goals of this study:

- Determine TDCu, TDZn, and their fluxes
- Determine Speciation of Cu, Zn and ligand fluxes
- Characterize ligands (Find K' , classes)
- Effect of bioturbation on fluxes
- Significance of benthic fluxes to overlying water of estuary

Methods

SAMPLING

- Collect with box corer (APRIL and JUNE, 2001)
- Transfer to core tubes
- Sample, Incubate 48-60 hours, Sample

ANALYTICAL

- Electrochemical Analysis
- Total Dissolved Cu and T.D. Zn – Std. Additions
- Speciation: CLE-CSV

Methods

SAMPLING

Sampling Site



Methods

SAMPLING

Box coring operations, *R/V Cape Fear*

The box corer



A typical
sediment core



Cores in incubator

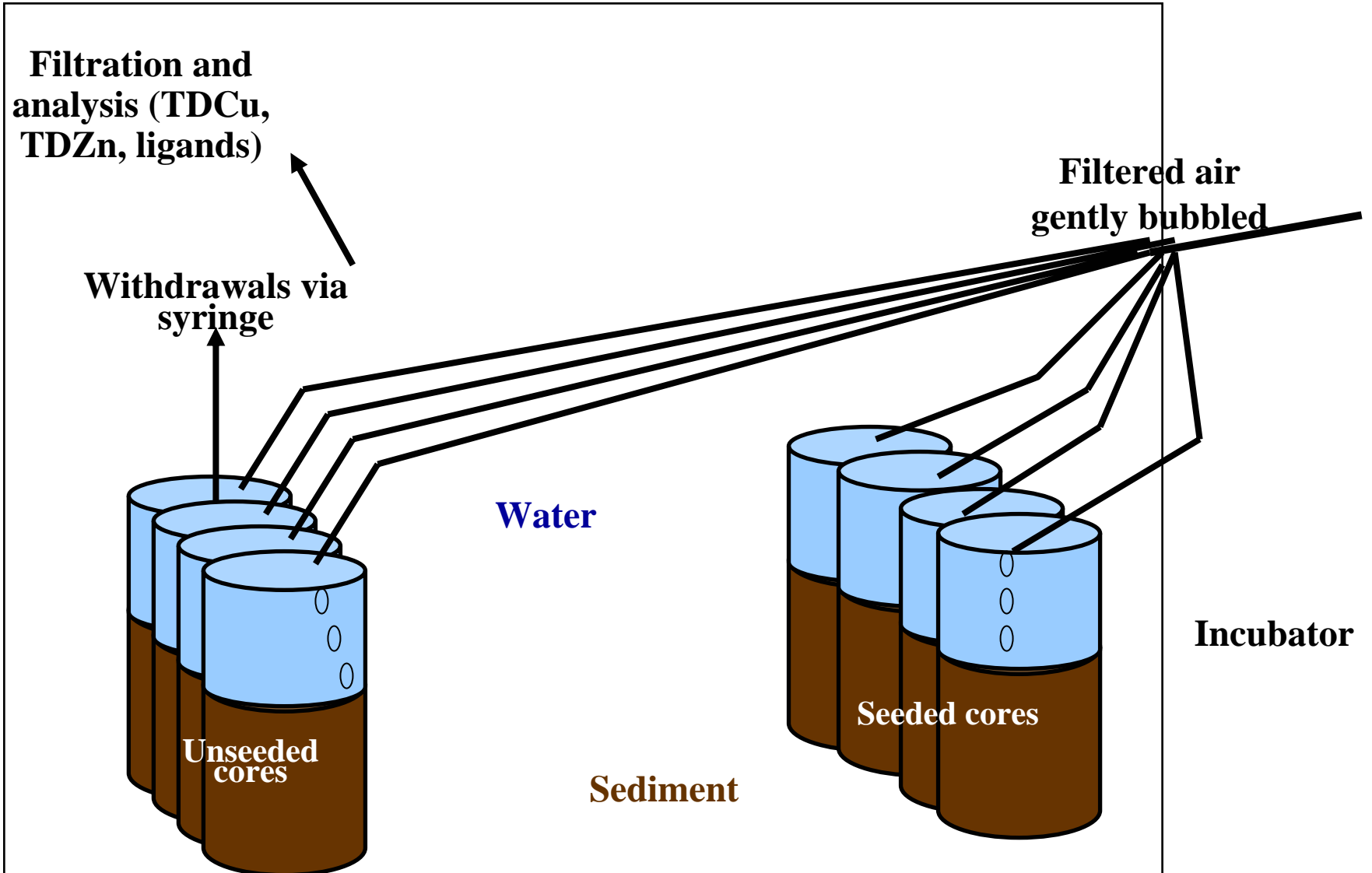
Methods

SAMPLING

Core incubation experiments



FLUX DETERMINATIONS

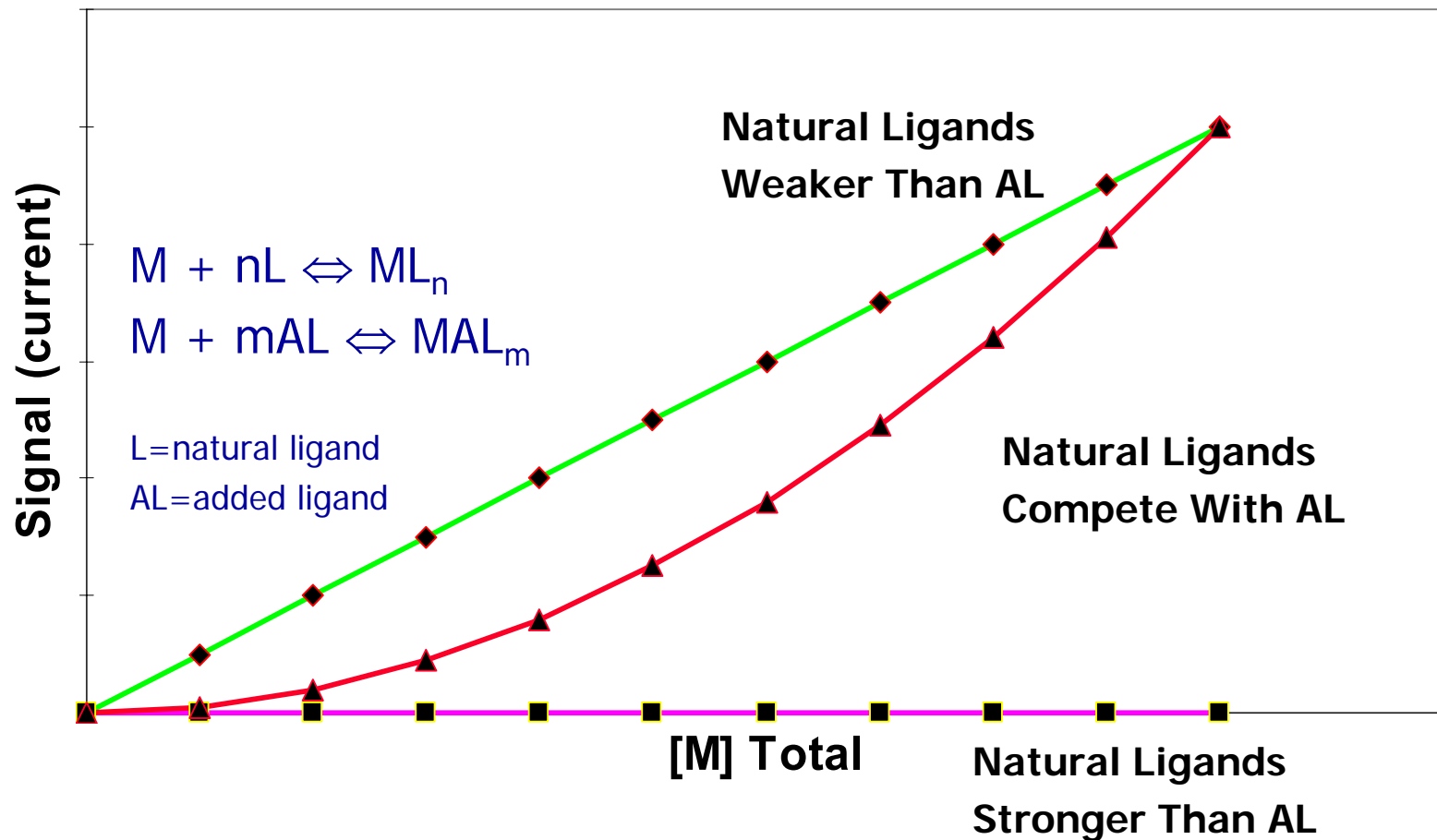


Methods

ANALYTICAL

CLE-CSV

Competitive Ligand Equilibration – Cathodic Stripping Voltammetry



Results

TDCu

April:

[TDCu] = 5 to 13 nM

Flux = 22 to -180 nmol·m⁻²·d⁻¹

June:

[TDCu] = 7 to 11 nM

Flux = 130 to -24 nmol·m⁻²·d⁻¹

TDZn

April:

[TDZn] = 5 to 12 nM

Flux = -56 to -300 nmol·m⁻²·d⁻¹

June:

[TDZn] = 6 to 11 nM

Flux = 56 to -245 nmol·m⁻²·d⁻¹

Results: Comparison

Location	[TDCu] (nM)	[TDZn] (nM)
Scheldt	10	50
Scheldt	10-20	10-50
Sabine	10-15	15-20
San Francisco Bay	27-30	6-12
Tamar	40	-
Humber	-	120-150
Ribble	25	-
Galveston Bay	-	10-13
Cape Fear	5-10	15-45
Cape Fear	5-13	5-12

Results

Seasonality: TDM Fluxes

- No difference in TDZn Fluxes
- APRIL TDCu fluxes greater than those in JUNE

(95% Confidence Level; Mann-Whitney test)

Results

Effect of Bioturbation: TDM Fluxes

- No difference in TDZn fluxes of seeded vs. unseeded cores
- UNSEEDED TDCu fluxes greater than SEEDED fluxes (June only)

(90% Confidence Level)

Results

[Cu- L]

April:

[L] = 75 to 95 nM

Flux = -160 to -1030 nmol·m⁻²·d⁻¹

June:

[L] = 52 to 102 nM

Flux = 587 to -813 nmol·m⁻²·d⁻¹

[Zn-L]

April:

[Zn-L] = 43 to 80 nM

Flux = 1221 to -531 nmol·m⁻²·d⁻¹

June:

[Zn-L] = 55 to 92 nM

Flux = 714 to -979 nmol·m⁻²·d⁻¹

Results: Comparison

Location	[L] (nM)	[L] (nM)
Scheldt	40-160	100
Tamar	200	150
Humber	-	80
Ribble	500	-
Cape Fear	52-102	55-92

Results

Seasonality: Ligand Fluxes

- No difference in fluxes of Cu-binding or Zn-binding ligands
(95% Confidence Level)

Bioturbation: Ligand Fluxes

- No difference in fluxes between seeded and unseeded cores
(90% Confidence Level)

Implications

- **CFE: short residence time**
- **Benthic fluxes account for less than 5% of standing stock of TDCu, TDZn, [Zn-L], and [Cu-L] in CFE water column**
- **These same fluxes could be significant in another estuary if similar sediments, but longer residence time**
- ***S. benedicti* not an influence on fluxes**

Future Work

Modify titration concentrations to

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