



Knauss Lecture Series

12—1 PM Wednesday December 8, 2010

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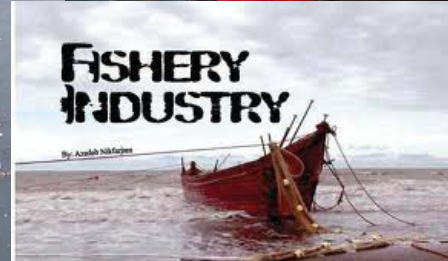
Transport of contaminants from
sediments to the water column and
environmental remediation strategies

Priscilla Viana

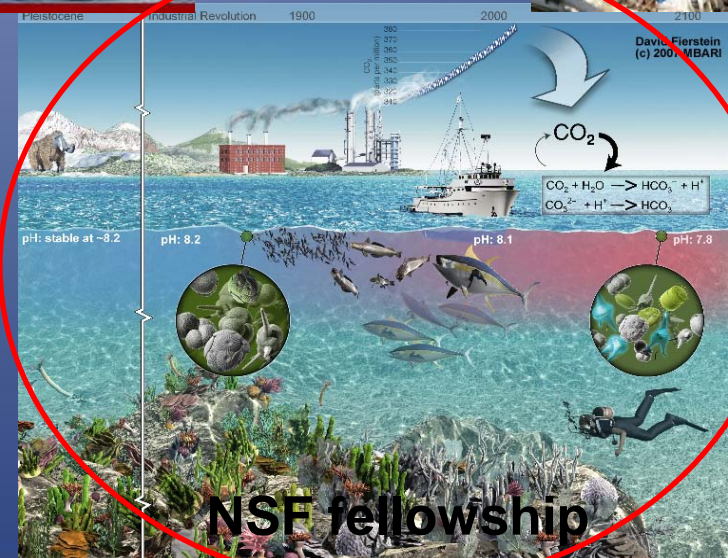
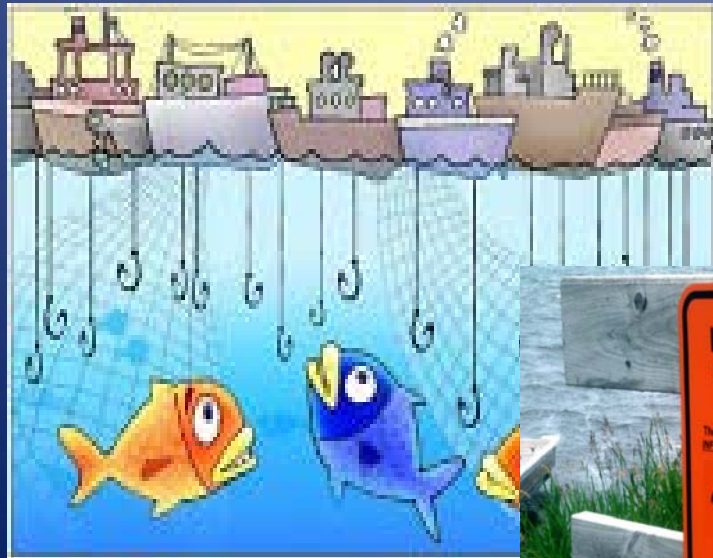
December 8th, 2010

Why should we care?

- Should future generations pay for our actions?



Environmental Stressors



Remediation of Contaminated Sediments: Capping + Additives



- To stimulate degradation
 - Add organisms
- To stimulate sequestration
 - Add sequestration additives
 - Add hydraulic barrier

Sequestration additives

- OC and GAC: efficient for organics
 - modified → metal sequestration

- OC: SA, hydraulic conductivity, CEC

(Alther 2001, Knox et al. 2008, Reible et al. 2007, Viana et al. 2008)

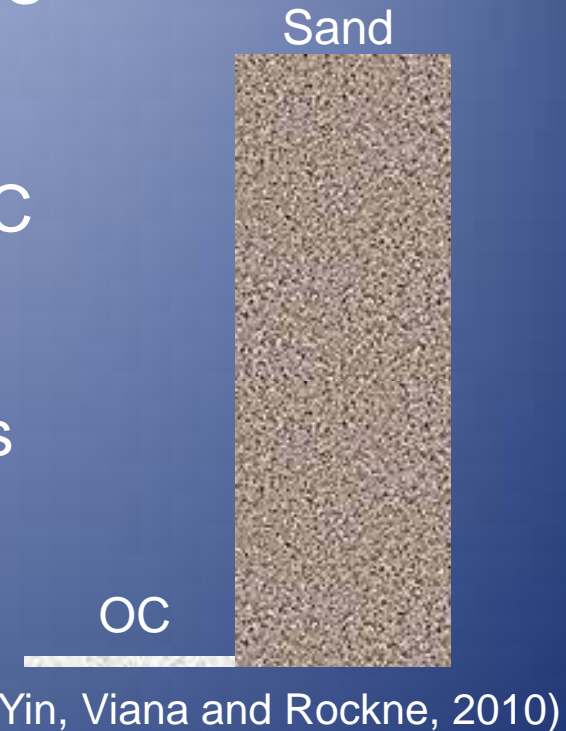
- GAC: impregnated with anionic surfactant to adsorb cationic metals

- Apatite: binds metals into insoluble phases – stable

– Replace Ca^{2+} , PO_4^{3-} ions

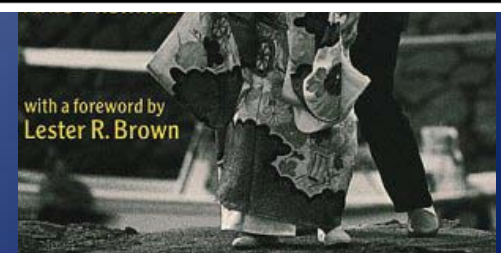
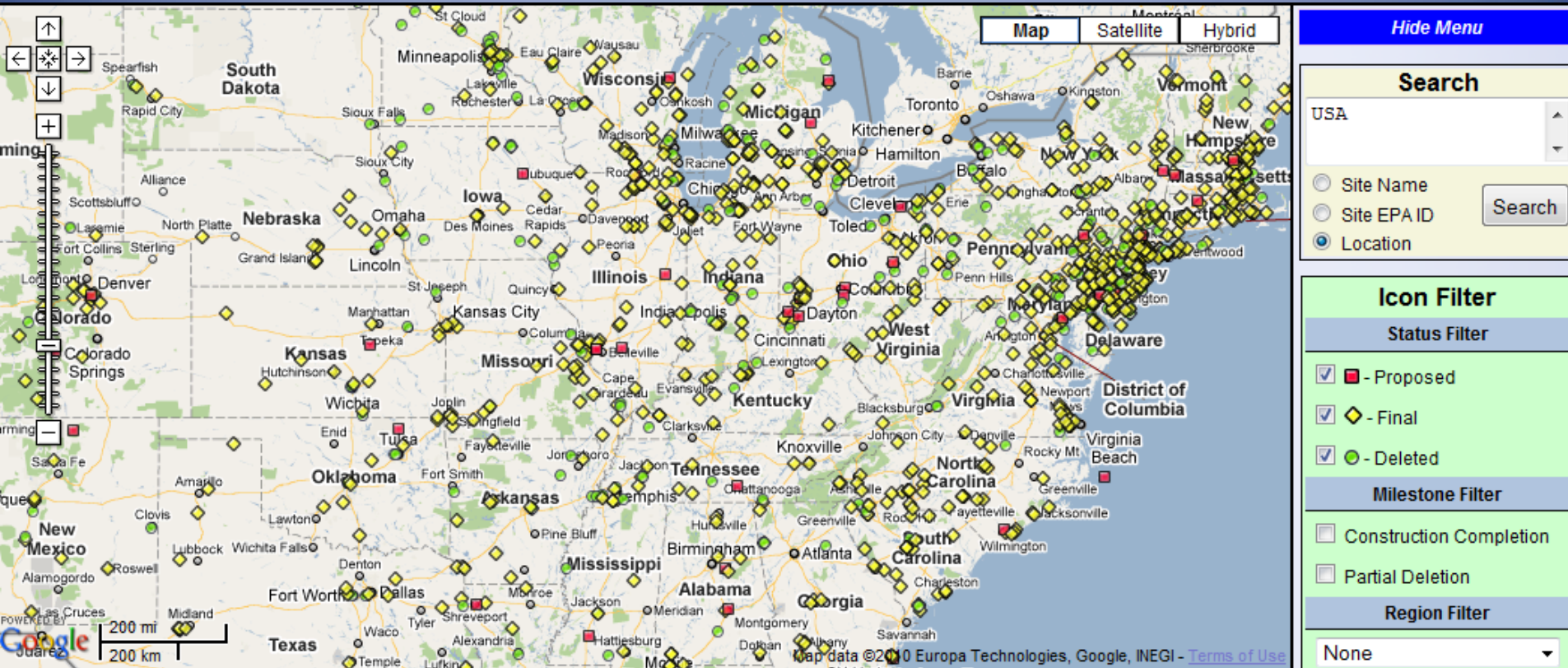
– $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$

(Bostick et al. 2003, Crannel et al. 2004, Kaplan and Knox 2004, Roberts 2004)

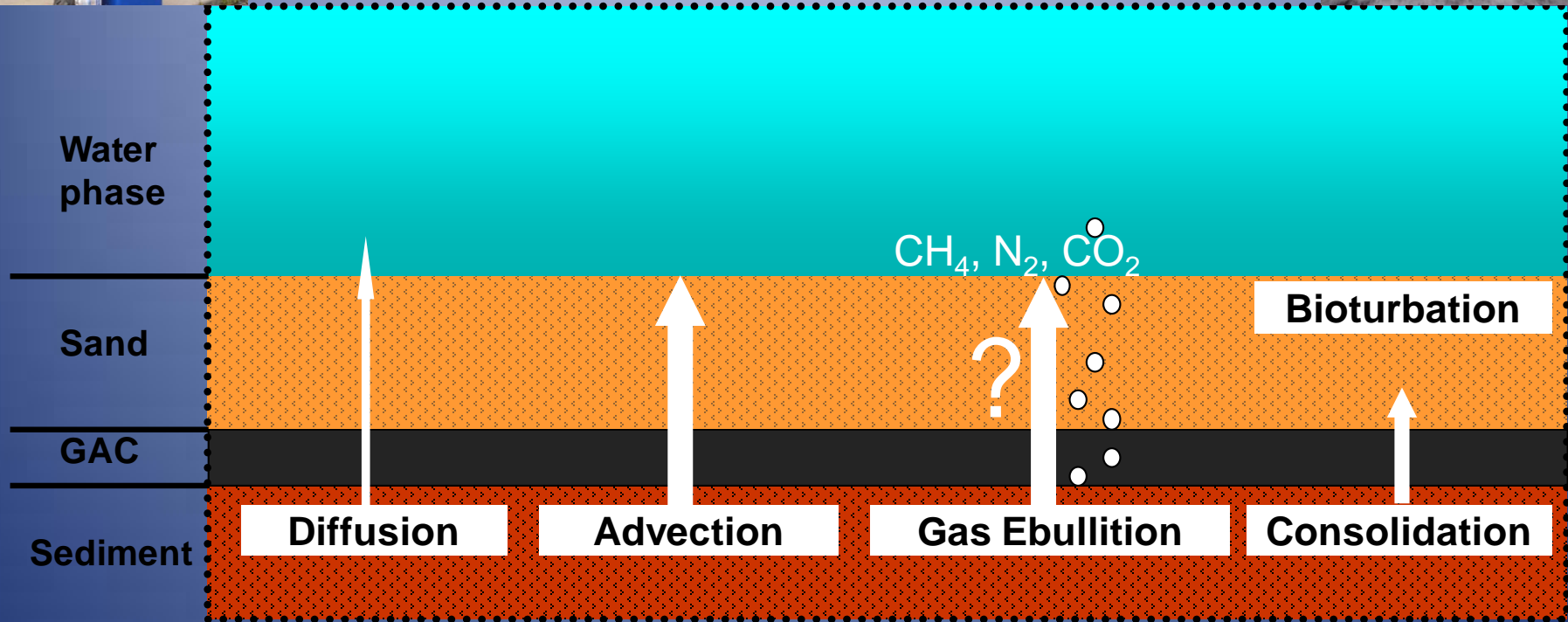


Motivation – Haz. Waste Sites

- Handful of “megasites” > \$2 billion (US) each



Transport Processes



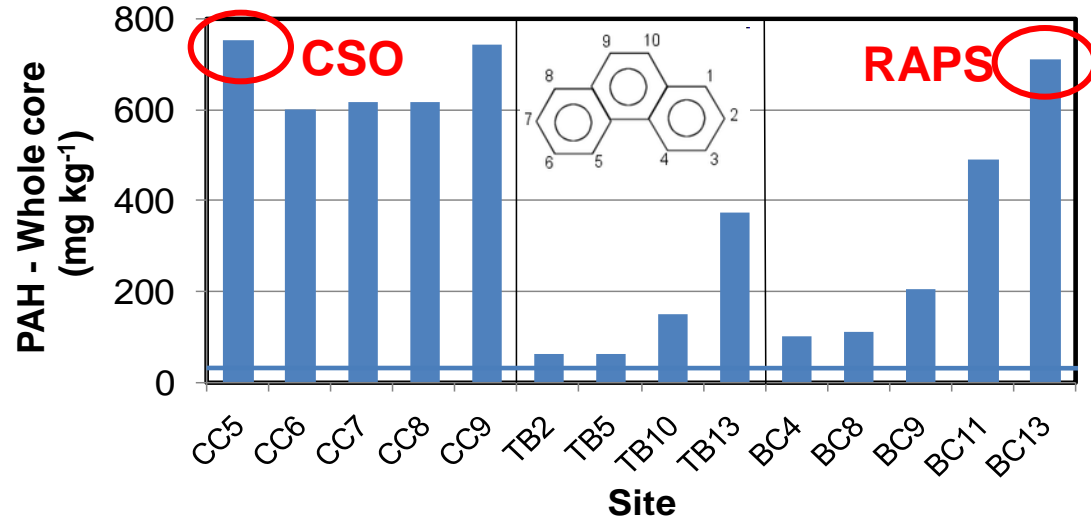
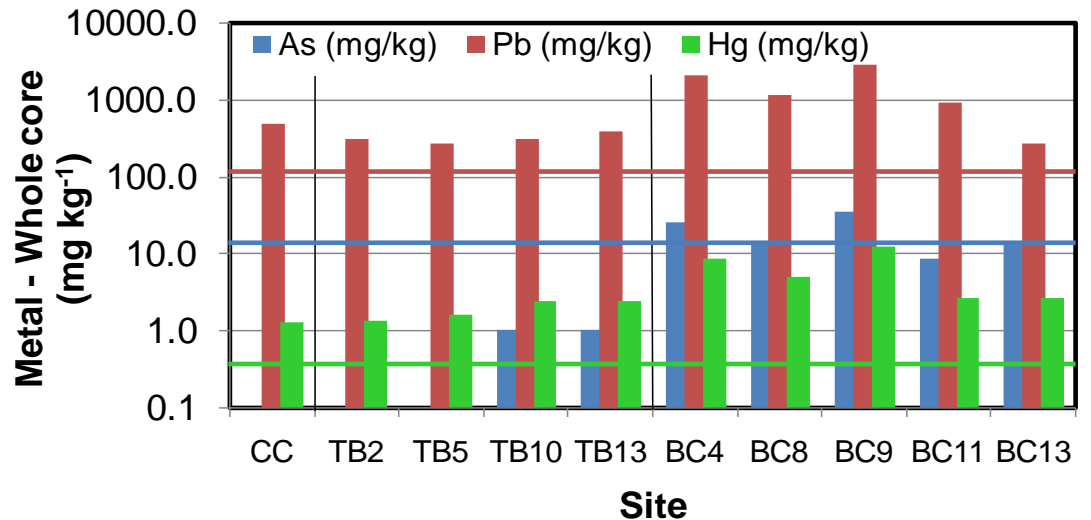
$$f(K_d, D_{mol}, \theta, \rho, \text{cap thickness}, K_h, d_h/d_x)$$

- GE: Methanogenic OM degradation + denitrification
 - Cap integrity: deflections ~ **0.75 m, 30–45 d** (Reible et al., 2006)

Objectives

1. Benthic flux chamber and gas ebullition studies: ≠
Ts and sites in the Chicago River (w/o capping)
 - Quantify the transport of contaminants
 - **Develop a model to predict** the transport of contaminants due to gas ebullition
2. Model the transport of contaminants through OC, AP, GAC and sand
 - Capping performance: Compile model parameter data + Monte Carlo for uncertainty
3. **Isotherm experiments and column studies**
4. Design an active capping demonstration project

Chicago River



Horizontal colored lines: NOAA guidelines for fresh water contaminated sediments (Upper Effects Threshold, SQuiRTs)

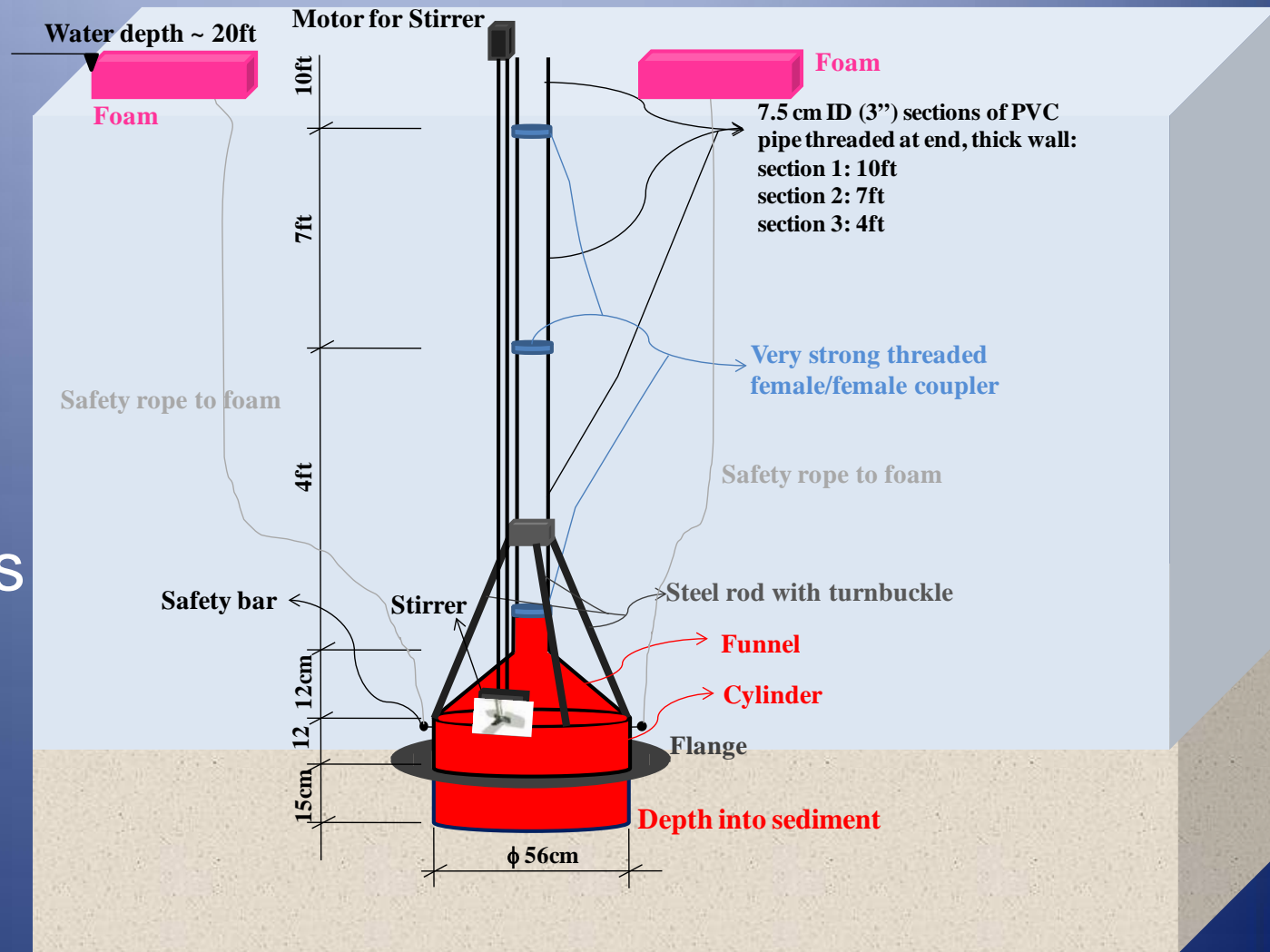
1. Site Characterization, Benthic Flux and Gas Ebullition Studies

- Sample collection
 - 14 surface grabs/14 cores
- OM content: LOI at 375 °C
- OC analyses: EA
 - Predictor of sorption/oxidant demand
- Anions: IC
 - Predictor of microbial oxidant activity
- PAHs: GC/MS (Soxhlet extraction)
- PCBs:
 - USEPA method 8082 (USACE)
- Metals: ICP-MS
 - USEPA method 6010B



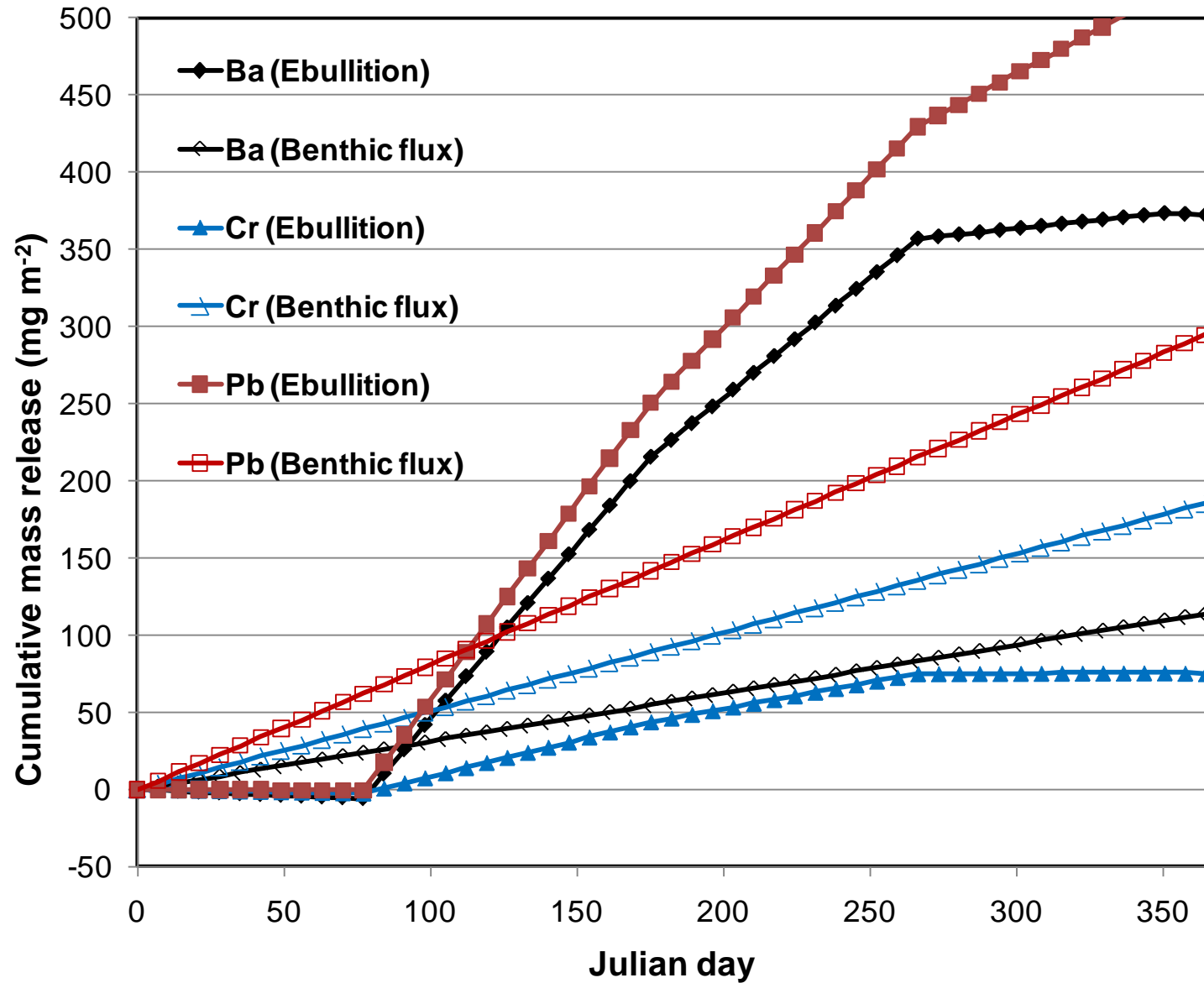
Benthic Flux Chamber Schematic

- PAH
- Metals
- Sulfide
- Ammonia
- Nitrate
- DOC
- Phosphorous
- Water pH
- DO
- ORP

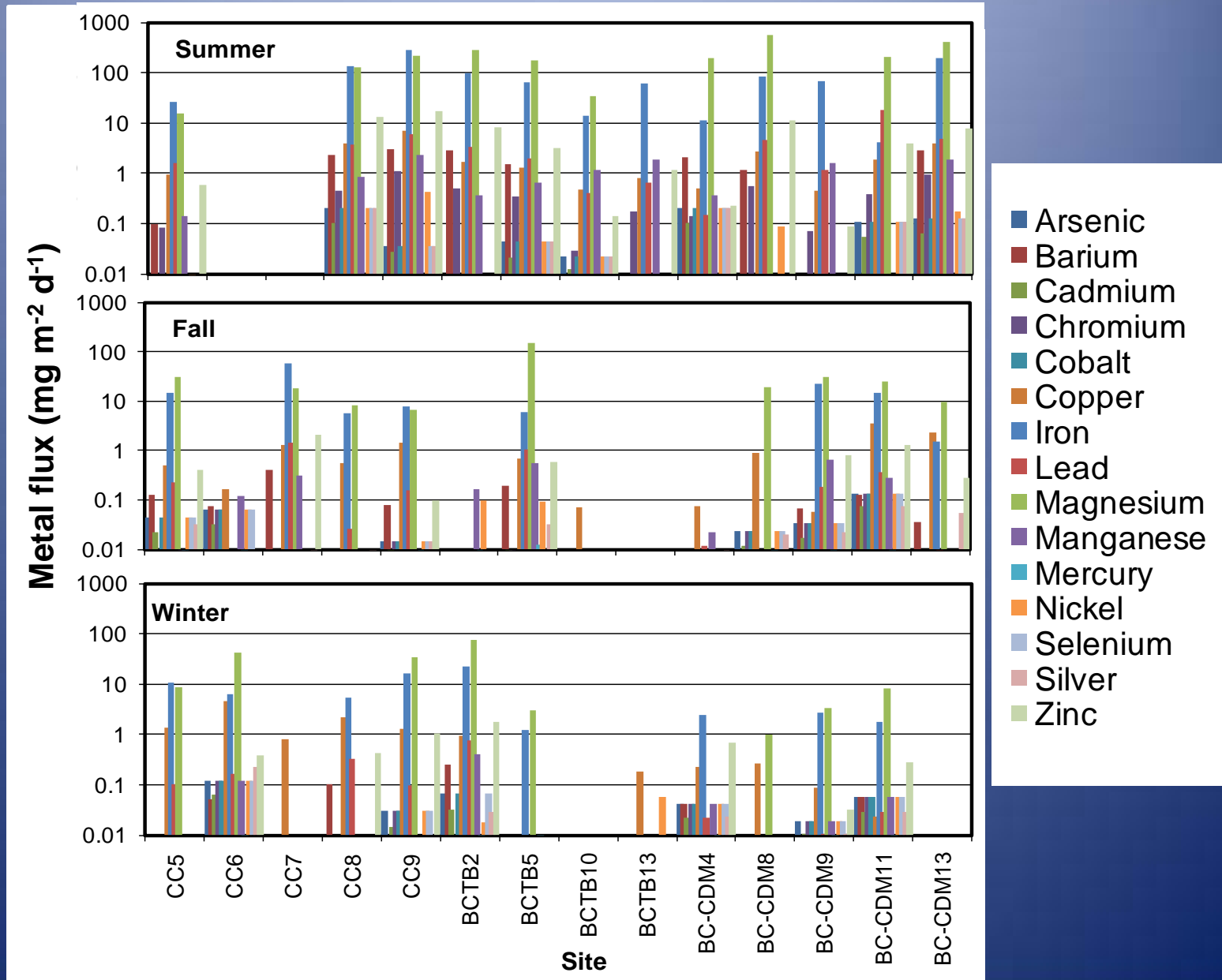


Compare with contaminant flux due to gas ebullition and after capping (simulations + real results after cap placement)

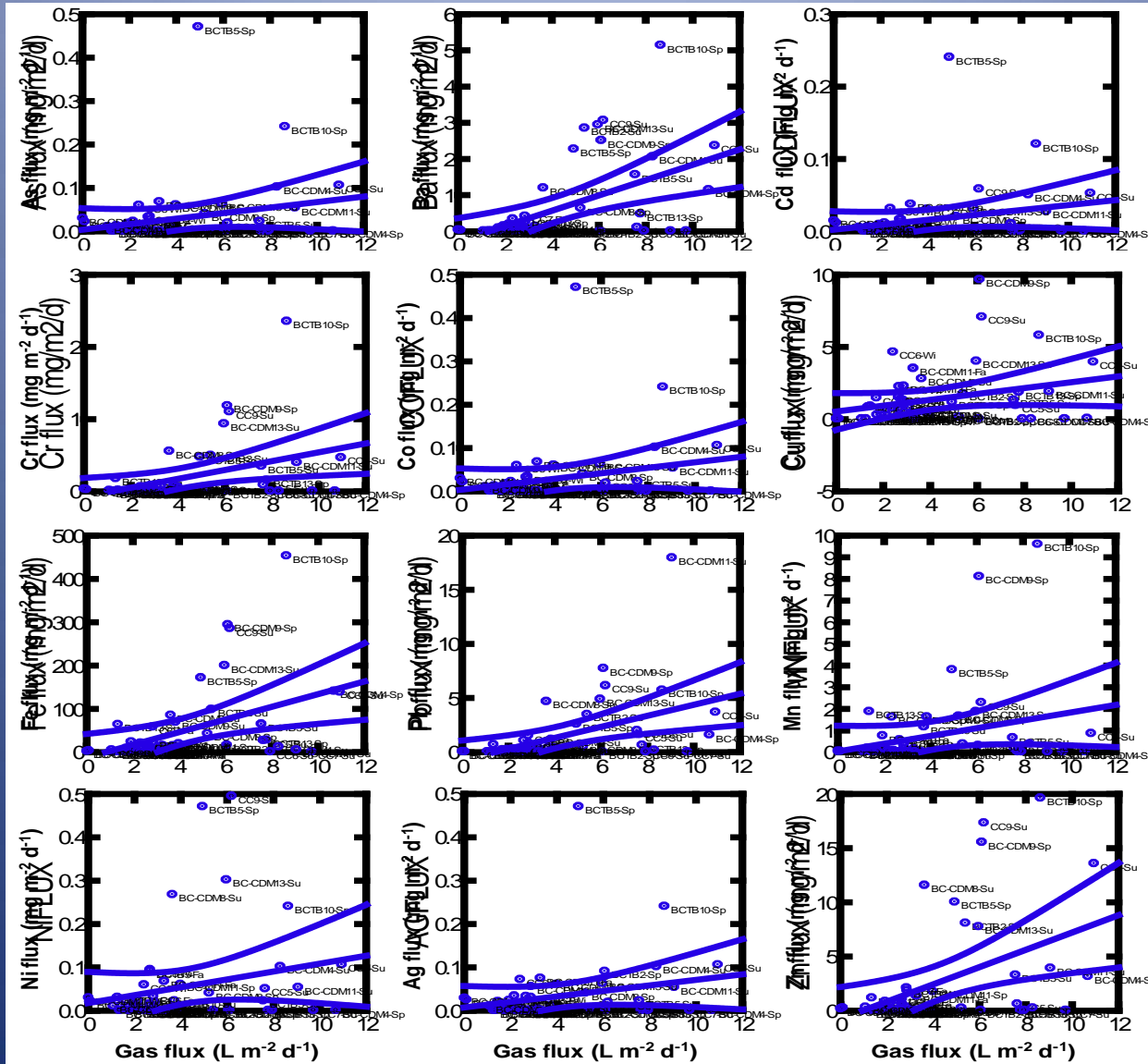
Transport of Contaminants



Ebullition-Facilitated Metal Flux



Model Ebullition-Facilitated Contaminant Flux (w/o Capping)



Conclusions

- Ebullition-facilitated metal fluxes were surprisingly large: 2 to 490 mg m⁻² d⁻¹ (for Cr and Fe, respectively)
- Ebullition-facilitated contaminant transport: significant contribution on the total contaminant flux from sediments to the water column
 - Principles governing transport are different
 - Metals: Particle re-suspension (total gas flux)
 - Organics: Contaminant partitioning and sorption into/onto the gas bubbles (total gas flux + OC)

2. Model Contaminant Transport with Capping

- Diffusion

$$\frac{C}{C_o} = \text{erfc} \left(\frac{x}{2\sqrt{D_{mol}\theta_e^{7/3}}} \frac{\sqrt{\theta_e + \rho K_d}}{\sqrt{t}} \right)$$

$$c(x,t) = c_o \text{erfc} \left(\frac{x}{\sqrt{4D_{obs}t}} \right)$$

$$D_{obs} = \frac{D_{mol} \cdot \tau}{R}$$

$$R = 1 + k_d \cdot \rho_b / \phi_e$$

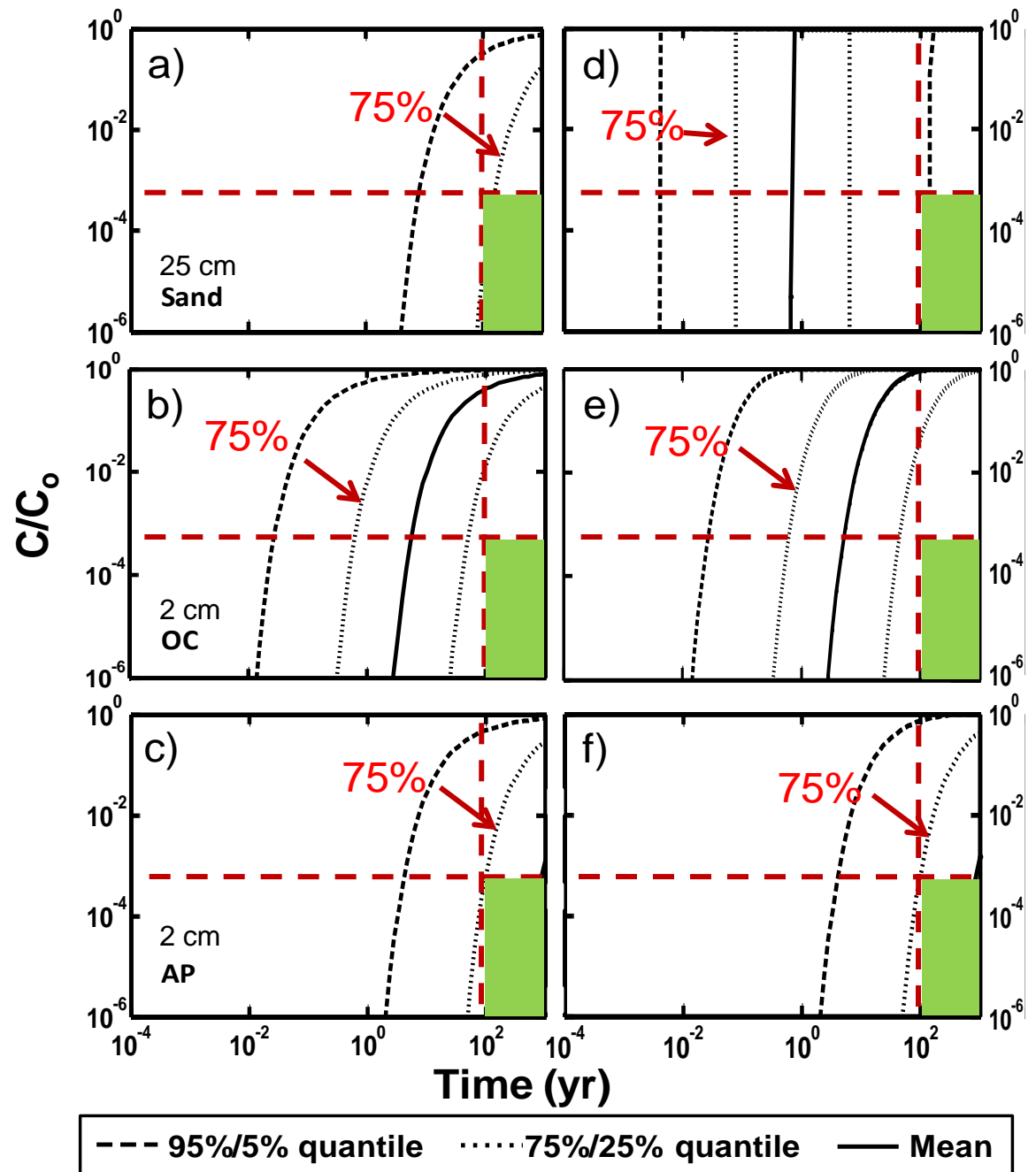
Ratio between $C(x,t)$ - the breakthrough porewater concentration of contam. at the top of the cap at time t and C_o - the initial concentration of contam. in the sediment porewater

- Advection

$$\frac{C}{C_o} = \frac{1}{2} \left(\text{erfc} \left(\frac{x\sqrt{(\theta_e + \rho K_d)}}{2\sqrt{D_{mol}\theta_e^{7/3}}\sqrt{t}} - \frac{k_h}{\sqrt{(\theta_e + \rho K_d)}} \frac{d_h/d_x}{2\sqrt{D_{mol}\theta_e^{7/3}}} \sqrt{t} \right) + \dots \right. \\ \left. \exp \left(\frac{xk_h(d_h/d_x)}{D_{mol}\theta_e^{7/3}} \right) \text{erfc} \left(\frac{x\sqrt{(\theta_e + \rho K_d)}}{2\sqrt{D_{mol}\theta_e^{7/3}}\sqrt{t}} + \frac{k_h}{\sqrt{(\theta_e + \rho K_d)}} \frac{d_h/d_x}{2\sqrt{D_{mol}\theta_e^{7/3}}} \sqrt{t} \right) \right)$$

Monte Carlo: assess capping performance to minimize **Cd** release and account for data uncertainties.

Shown are simulations under **diffusion** (a, b, c) and **advective** (d, e, f) conditions in sand (a, d), organoclay (b, e) and apatite (c, f)



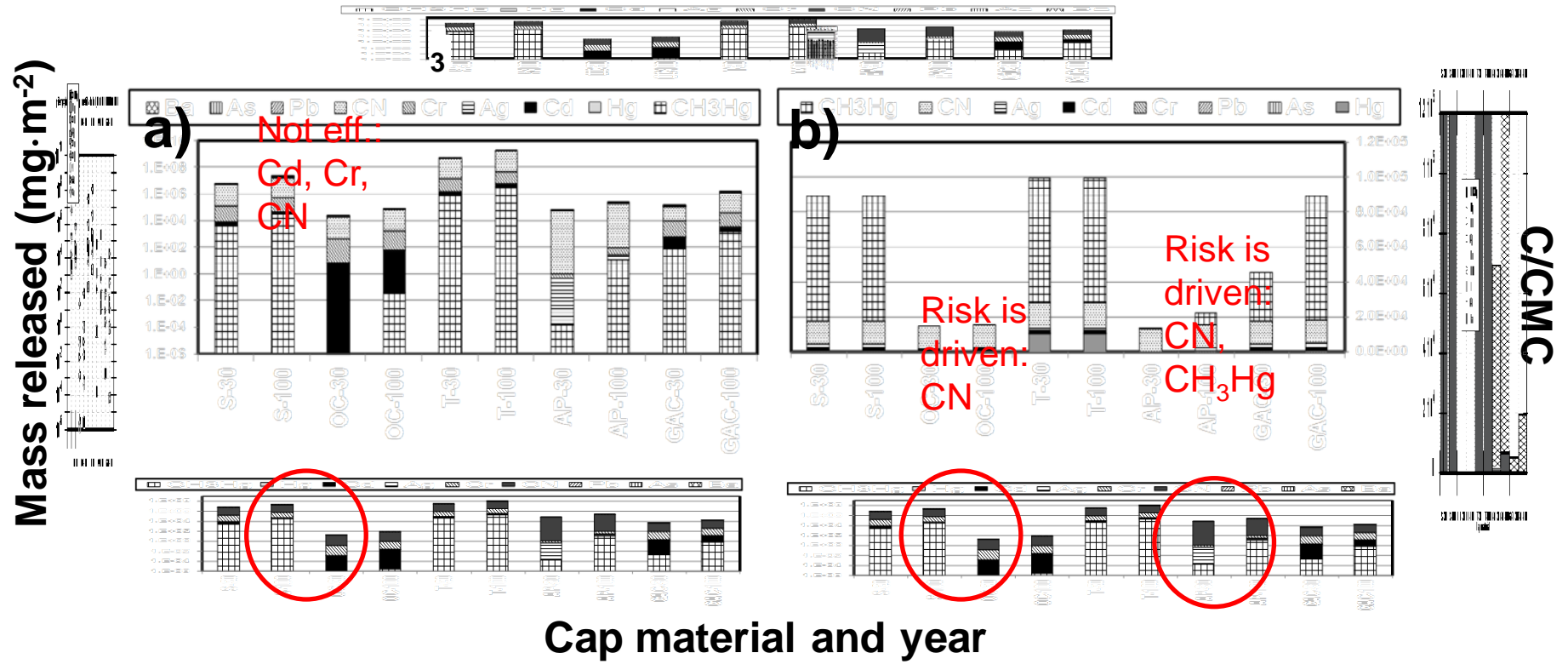
(Viana et al., 2008)

Summary of Monte Carlo study: Cap performance

Compound	Capping material									
	Sand		OC		Tires		AP		GAC	
	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC
Cd, pH 7	++/-	++/-	-/-	-/-	-/-	-/-	+++/>			

^a - means cap complies with the USEPA CMC or CCC after 100 yr within <50% CI; +, ++ and +++ means cap complies with the CMC or CCC within mean, 75% and 95% CI, respectively. First symbol means result for diffusion, second symbol means result for advection ($d_h/d_x=0.05$). n.a.=there is no EPA CCC criteria for the compound

Cum. Areal Mass Release and Conc. Normalized to CMC



Simulated total mass released and toxicity-normalized concentration measures of contaminant release after 30 and 100 yrs under advection flow conditions ($d_h/d_x=0.05$) through cap materials. Shown are: (a) Cumulative areal mass release and (b) Contaminant concentration data at the cap surface normalized to the toxicity criteria for maximum concentration (CMC) from EPA

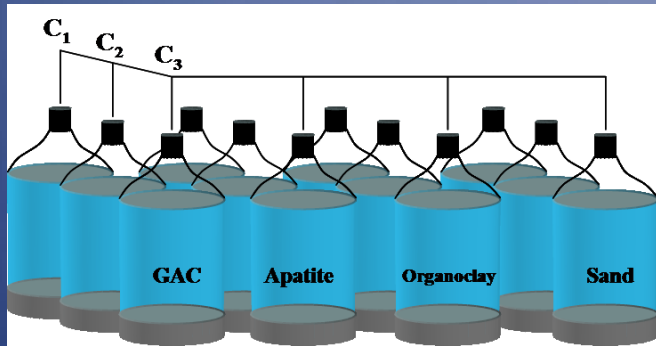
Conclusions and Implications

- Cap thickness: most important factor in diffusion
- Advection: $\downarrow k_h$ as or more important than $\uparrow K_d$
 - More K_d data under realistic field conditions
- Apatite: perform best for Cd, Pb and Hg
- OC: perform best for Ag, As, Ba, CH_3Hg , Hg
- No cap is predicted to be effective for Cr and CN (under these x)
- Cap combinations
 - Apatite or OC mat + sand



3. Isotherm + Column Experiments

- Lab studies: compare to model simulations
 - Measure θ , ρ , k_h , K_d and time for contaminant breakthrough

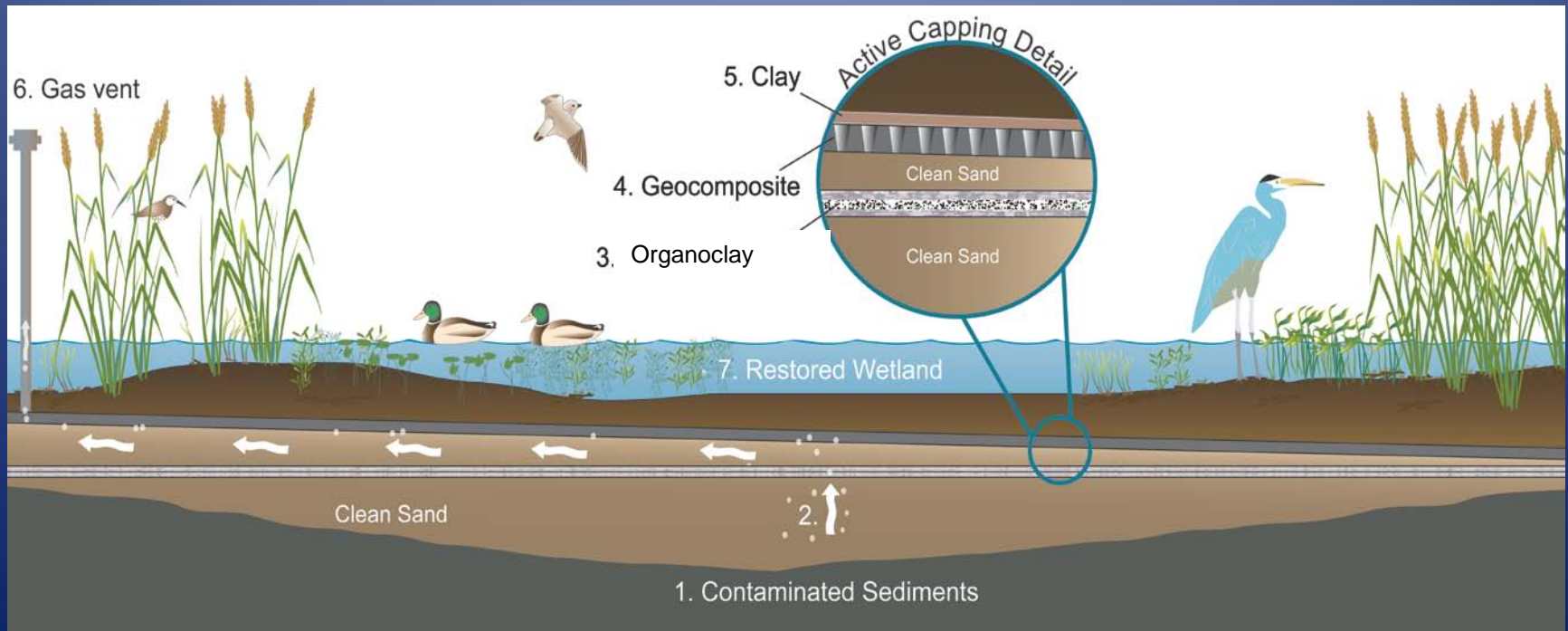
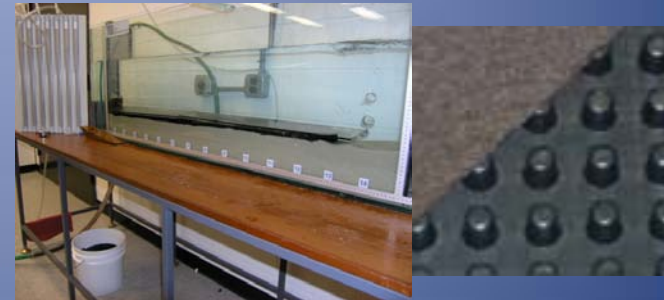


Metal solution \rightarrow adjusted pH \rightarrow added capping material \rightarrow sparged w/ N_2 \rightarrow 5 weeks in the dark, 20° C \rightarrow concentration in the water and in the sorbent

(1) feed vessel containing metal influent solution, (2) peristaltic feed pump, (3) upstream and downstream pressure gauges, (4) test column (10 cm by 1 or 1.5 cm) and (5) effluent graduated cylinder to measure volume of sample

4. Geo-Engineering Strategies to Mitigate Water and Sed. Poll.

- Active capping demonstration project
 - High OM: gas collection system



Knauss Sea Grant Fellow at the NSF

- OA, EID in marine systems, and scientific coordination related to the DWH oil spill:
 - EID and OA programs: Proposal review process
 - IWG-OA: Develop an inter-agency SRP for OA as mandated by Congress (FOARAM Act)
 - Developing a workshop and a special session on EMID at the 2011 ASLO meeting (February 2011)
 - <https://sites.google.com/site/emidworkshop/>

Knauss Sea Grant Fellow at the NSF

- OA, EID in marine systems, and scientific coordination related to the DWH oil spill:
 - Coordinating an inter-agency research conference on the DWH oil spill (October 2010)
 - <http://www.marine.usf.edu/conferences/fio/NSTC-JSOST-PI/index.shtml>
- Multiple presentations at the Eco-DAS symposium: own research and Fellowship activities (October 2010)

Ocean Acidification: IWG on OA

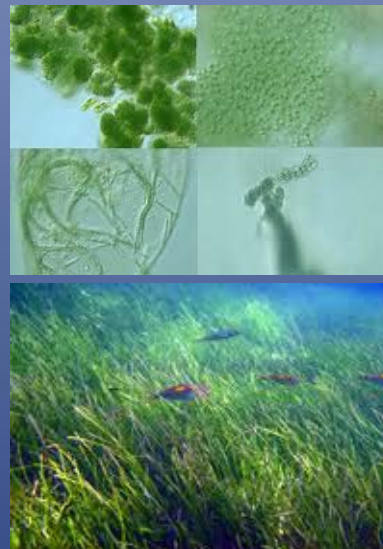
- SRP: monitoring, research and modeling priorities
- How will ecologically or economically important organisms respond to OA?
 - Calcifying x non-calcifying organisms (whole-organism approach)

NEG.



(Hoegh-Guldberg et al., 2007; Kuffner et al., 2008; Royal Society, 2005)

POS.



(Doney et al., 2009; Kranz et al., 2009)

????



(Calosi et al., 2009; Doney et al., 2009; Langer et al., 2006)

- How changes at the organism level will alter ecosystem structure and function? (Falkowski and Oliver, 2007)

- What is the potential for physiological acclimation and adaptation?

- Paleo-reconstruction
- Seafloor vents: emit CO₂ at ambient T
- Regions with naturally varying pH gradients (coastal upwelling systems)



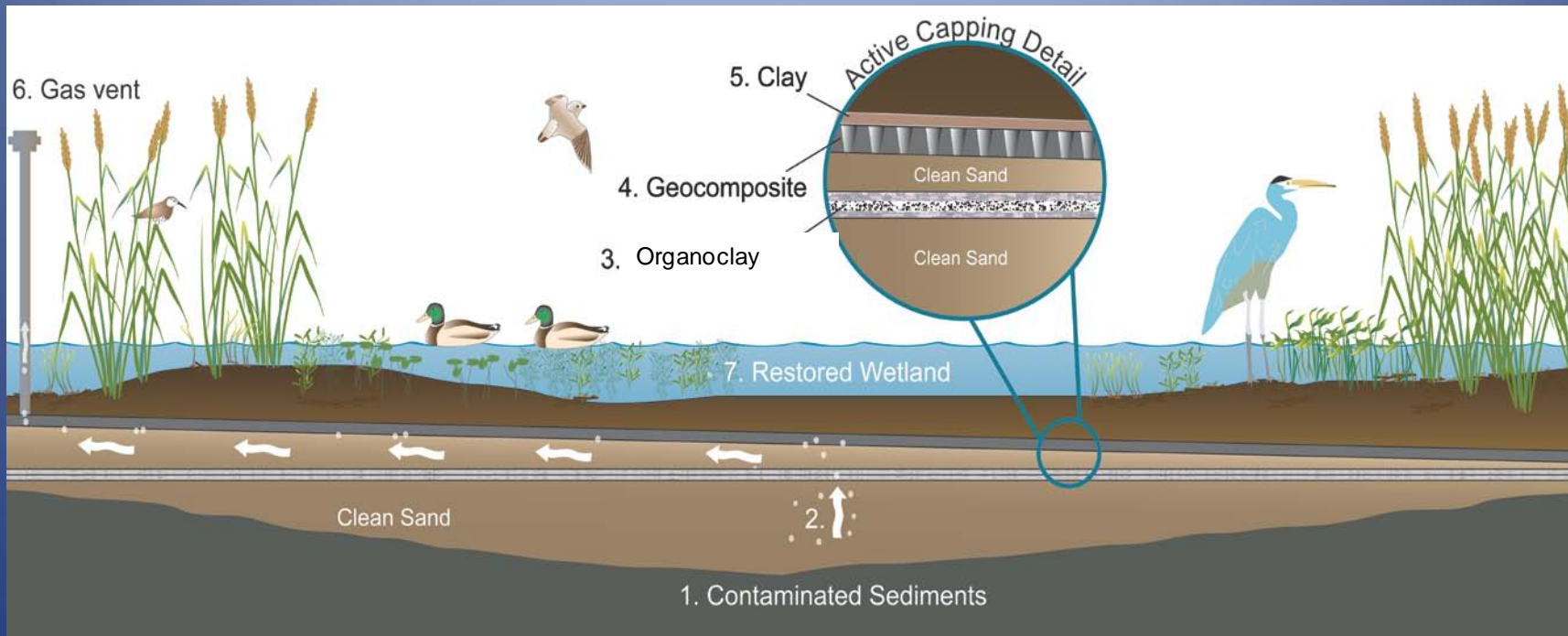
- What is the effectiveness of available mitigation strategies? Side effects?

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Environmental Restoration Project



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References

1. Alther, G. R. Organoclays remove organic and metals from water. In *The Annual International Conference on Soils, Sediments, Water and Energy*; University of Massachusetts at Amherst, 2001.
2. Bostick, W. D.; Stevenson, R. J.; Harris, L. A.; Peery, D.; Hall, J. R.; Shoemaker, J. L.; Jarabek, R. J.; Munday, E. B. Use of apatite for chemical stabilization of subsurface contaminants; DE-AD26-01NT41306; Materials and Chemistry Laboratory, Inc.: Oak Ridge, TN, 2003.
3. Charbeneau, R. J. *Groundwater Hydraulics and Pollutant Transport*; Prentice Hall: Upper Saddle River, NJ, 2000.
4. Costello, M.; Talsma, D. Remedial design modeling at a superfund sediment site; <http://www.serviceenv.com/Web2005/Docs/Paper42byCostello.pdf>, 2005.
5. Crannell, B. S.; Eighmy, T. T.; Willson, C.; Reible, D. D.; Yin, M. Pilot-scale reactive barrier technologies for containment of metal-contaminated sediments and dredged materials; Submitted to NOAA/UNH Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET), 2004.
6. Hughes, J. B.; Valsaraj, K. T.; Willson, C. S. In-situ containment and treatment: Engineering cap integrity and reactivity; HSRC/S&SW, Georgia Institute of Technology and Louisiana State University, 2005.
7. Kaplan, D. I.; Knox, A. S. Enhanced contaminant desorption induced by phosphate mineral additions to sediment. *Environ. Sci. Technol.*, 2004, 38, 3153-3160.
8. Knox, A. S.; Paller, M. H.; Reible, D. D.; Ma, X.; Petrisor, I. G. Sequestering agents for active caps - Remediation of metals and organics. *Soil Sediment Contam.*, 2008, 17, 516 - 532.

9. Koretsky, C. M.; Haas, J. R.; Miller, D.; Ndenga, N. T. Seasonal variations in pore water and sediment geochemistry of littoral lake sediments (Asylum Lake, MI, USA). *Geochem. Trans.* 2006, 7, 11.
10. Reible, D.; Lu, X.; Moretti, L.; Galjour, J.; Ma, X. Organoclays for the capping of contaminated sediments. In *AICHE Annual Meeting*; Salt Lake City, UT, 2007.
11. Reible, D.; Lampert, D.; Constant, D.; Mutch-Jr., R. D.; Zhu, Y. Active capping demonstration in the Anacostia River, Washington, D.C. *Remediation J.*, 2006, 17, 39-53.
12. Roberts, K. L. Modeling of river hydrodynamics and active cap effectiveness in the Anacostia River; Louisiana State University; Master of Science in Civil Engineering Thesis, 2004.
13. Viana, P. Z.; Yin, K.; Rockne, K. J. Contaminant-facilitated transport due to sediment gas production: Laboratory and field studies. In *Fifth International Conference on Remediation of Contaminated Sediments*; Jacksonville, FL, 2009.
14. Viana, P. Z.; Yin, K.; Rockne, K. J. Modeling active capping efficacy. 1. Metal and organometal contaminated sediment remediation. *Environ. Sci. Technol.* 2008, 42, 8922-8929.
15. Viana, P. Z.; Yin, K.; Zhao, X.; Rockne, K. J. Active sediment capping for pollutant mixtures: Control of biogenic gas production under highly intermittent flows. *Land Contam. Reclamation*, 2007, 15, 413-425.
16. USEPA. Partition coefficients for metals in surface water, soil, and waste; EPA/600/R-05/074; U. S. Environmental Protection Agency: Washington, DC, 2005.
17. USEPA. Understanding variation in partition coefficient, K_d , values; EPA 402-R-99-004B; U. S. Environmental Protection Agency: Washington, DC, 1999.
18. Yin, K.; Viana, P. Z.; Rockne, K. J. Verification of active cap contaminant breakthrough simulations via laboratory column studies. In *Fifth International Conference on Remediation of Contaminated Sediments*; Jacksonville, FL, 2009.

19. Calosi, P., Donohue, P., Alber, S., and Spicer, J. I. Synergistic effect of ocean acidification and elevated temperature on the physiological ecology of the intertidal crab *Porcellana platycheles*. *Comparative Biochemistry and Physiology – Part A*, 2009, 153 (2):169. Abstracts of the Annual Main Meeting of the Society of Experimental Biology, 28th June – 1st July, Glasgow, UK.
20. Doney, S. C., W. M. Balch, V. J. Fabry, and R. A. Feely. Ocean acidification: A critical emerging problem for the ocean sciences. *Oceanography*, 2009, 22 (4): 16-25.
21. Falkowski, P. G. and M. J. Oliver. Mix and match: How climate selects phytoplankton. *Nat. Rev. Micro.*, 2007, 5 (10): 813-819.
22. Hoegh-Guldberg, O., P. J. Mumby, A. J. Hooten, R. S. Steneck, P. Greenfield, E. Gomez, C. D. Harvell, P. F. Sale, A. J. Edwards, K. Caldeira, N. Knowlton, C. M. Eakin, R. Iglesias-Prieto, N. Muthiga, R. H. Bradbury, A. Dubi, and M. E. Hatziolos. Coral Reefs Under Rapid Climate Change and Ocean Acidification. *Science*, 2007, 318 (5857): 1737.
23. Kleypas, J. A., R. W. Buddemeier, D. Archer, J.-P. Gattuso, C. Langdon, and B. N. Opdyke. Geochemical Consequences of Increased Atmospheric Carbon Dioxide on Coral Reefs. *Science*, 1999, 284 (5411): 118-120.
24. Kranz, S.A., D. Sültemeyer, K.-U. Richter, and B. Rost. Carbon Acquisition by *Trichodesmium*: the Effect of pCO₂ and Diurnal Changes. *Limnology and Oceanography*, 2009, 54 (2): 548-559.
25. Kuffner, I. B., A. J. Andersson, P. L. Jokiel, K. U. S. Rodgers, and F. T. Mackenzie. Decreased Abundance of Crustose Coralline Algae due to Ocean Acidification. *Nature Geosci.*, 2008, 1 (2): 114-117.
26. Langer, G., M. Geisen, K. Baumann, J. Kläs, U. Riebesell, S. Thoms, and J. R. Young. Species-Specific Responses of Calcifying Algae to Changing Seawater Carbonate Chemistry. *Geochem. Geophys. Geosyst.*, 2006, 7: Q09006.

27. National Research Council – NRC. *Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean*. Committee on the Development of an Integrated Science Strategy for Ocean Acidification Monitoring, Research, and Impacts Assessment, Ocean Studies Board, Division on Earth and Life Studies, 2010.
28. Riebesell, U., V. J. Fabry, L. Hansson, and J.-P. Gattuso (Eds.). *Guide to Best Practices for Ocean Acidification Research and Data Reporting*. Publications Office of the European Union, Luxembourg, 2010, 260 pp.
29. Royal Society. *Ocean acidification due to increasing atmospheric carbon dioxide*. The Royal Society, 2005, London, UK, 68 pp.

Sediment Heterogeneity

Parameter	Value
Pb and Hg (mg/kg dry wt) (NOAA)	260 – 2,800 (127) , 1.2 – 12 (0.6)
PAHs (mg/kg) (NOAA)	60 – 750 (12)
GF_f (L m⁻² d⁻¹)	1.4 – 9.8
CH ₄ GF _f (L m ⁻² d ⁻¹)	0.8 – 6.7
VGPR _l (L m ⁻³ d ⁻¹)	1.8 – 18 (highest at CC5)
Temperature during study (°C)	23.5 - 27
SG OM (%)	1.5 – 32 (highest at CC5)
Whole Core OM (%)	5.5 - 26
SG OC (%)	1.5 – 20 (highest at CC5)
Whole Core OC (%)	0.6 - 15
Lab-derived E_a (kJ mol ⁻¹)	17 – 64 (lowest at CC5, OM diagenetically young)
Water depth (m)	1.2 – 5.5
Sediment depth to hardpan (m)	0.3 – 6.5
Gravel: Sand: Silt: Clay	(1 – 17%) : (9 – 89%) : (0.1 – 53%) : (3 – 37%)

Metal solubility from literature, USEPA CMC and CMC/C_s

Compound	P10 (mg·l ⁻¹)	P50 (=C _s) (mg·l ⁻¹)	P90 (mg·l ⁻¹)	Geom std dev	CMC (mg·l ⁻¹)	CMC/C _s target	CCC (mg·l ⁻¹)	CCC/C _s target
Cd, pH 7	0.008	3	1240	110	2.0 10 ⁻³	6.6 10 ⁻⁴	2.5 10 ⁻⁴	8.3 10 ⁻⁵
Cr, pH 7	0.021	20	20500	220	1.0 10 ⁻¹	4.8 10 ⁻³	2.9 10 ⁻²	1.4 10 ⁻³
Pb, pH 7	0.26	4	60	8	6.5 10 ⁻²	1.7 10 ⁻²	2.5 10 ⁻³	6.4 10 ⁻⁴
Ag	0.17	8	390	20	3.2 10 ⁻³	3.9 10 ⁻⁴	n.a.	
As	0.018	5	1470	80	3.4 10 ⁻¹	6.5 10 ⁻²	1.5 10 ⁻¹	2.9 10 ⁻²
Ba	0.67	60	5970	40	n.a.		n.a.	
Hg	0.002	15	101000	1000	1.4 10 ⁻³	9.5 10 ⁻⁵	7.7 10 ⁻⁴	5.2 10 ⁻⁵
CH ₃ Hg		100			1.4 10 ⁻³	1.4 10 ⁻⁵	7.7 10 ⁻⁴	7.7 10 ⁻⁶
CN	0.35	280	232000	190	2.2 10 ⁻²	7.7 10 ⁻⁵	5.2 10 ⁻³	1.8 10 ⁻⁵

P10, P50, P90 = percentiles; n.a.=there is no EPA CMC and/or CCC criteria for the compound

Parameter values considered in the Monte Carlo simulations

Cap material	x (m)	φ_e		ρ (kg L ⁻¹)		k_h (m·yr ⁻¹) ^a	
		μ	σ	μ	σ	μ (or μ_g)	σ (or σ_g)
Sand	0.25	0.31	0.03	2	0.3	21,000	27,000
Organoclay	0.02	0.36	0.07	1.8	0.35	10	207
Shredded tires	0.1	0.48	0.2	0.7	0.05	280,000	10
Apatite	0.02	0.44	0.02	1.7	0.1	22	25
GAC	0.02	0.45	0.11	0.6	0.12	60	26

^a Organoclay, shredded tires and GAC k_h values are reported as geometric mean (μ_g) and geometric standard deviation (σ_g)

Ocean Acidification

- CO₂: 280 to 379 ppm; CH₄: 715 to 1774 ppb
- pH: 8.2 to 8.1; Ωar in the tropics: ↓ 30% by 2050
(Kleypas et al., 1999)

