

The Role of Sediment Resuspension in the  
Remobilization of Particulate-Phase Metals from  
Coastal Sediments  
Supporting Information

Linda H. Kalnejais<sup>1\*</sup>, William R. Martin<sup>1</sup>, Richard P. Signell<sup>2</sup>, Michael H. Bothner<sup>2</sup>

<sup>1</sup>Woods Hole Oceanographic Institution, Woods Hole, MA 02543

<sup>2</sup>US Geological Survey, Woods Hole, MA 02543

\*Corresponding author present address: University of California, Berkeley

Earth and Planetary Sciences, McCone Hall, Berkeley CA 94720. email:linda\_k@alum.mit.edu

11 pages, 4 Figures, 5 Tables

December 19, 2006

## **Erosion Chamber and Shear Stress Calibration**

The erosion chamber is shown in Figure S-1. The imposed bottom shear stress is a function of the propeller rotation rate. Sieved sand was used to calibrate the chamber. The rotational rate of the propeller was incrementally increased until significant movement of sand grains was observed. The shear stress required to resuspend the known grain size was determined from a Shield's threshold curve. The Shields's parameter was assumed to have a 20% uncertainty [3]. The analytical formula fitted to the Shield's curve by Soulsby and Whitehouse and extended to finer grain sizes [4] was used to calculate the critical shear stress. The results of the calibration (Figure S-2) show a linear response between the rotation rate and shear stress at the sediment-water interface.

## **Sampling and Trace Metal Analysis**

The trace metal content of the sediment samples was determined at the United States Geological Survey in Denver following the method of Briggs and Meier [5]. Certified reference materials from the National Research Council of Canada, marine sediment BCSS-1 and MESS-1, lake sediments LKSD-3 and harbor sediment PACS-2, the National Institute for Science and Technology standard reference material NIST-2709 and U.S.G.S marine sediment reference material MAG-1 were all run with each batch of samples (up to 50 samples). The data for Fe, Mn, Cu, Ag and Pb were all within the published values for these elements. Replicate samples for Fe, Mn, Cu and Pb varied by less than 5% and varied by less than 10% for Ag.

The metal content of the particulate material on the filter membranes was determined with the total sediment digest method of Briggs and Meier [5] but the digestion and analysis were performed at the Woods Hole Oceanographic Institution. Unused filter membranes and empty vials were also taken through the procedure to determine the trace metal concentrations associated with the membranes and digestion procedures. A Finnigan Element 2 ICP-MS was used to quantify the digest concentrations, with 50 $\mu$ L of digest diluted with

# Erosion Chamber

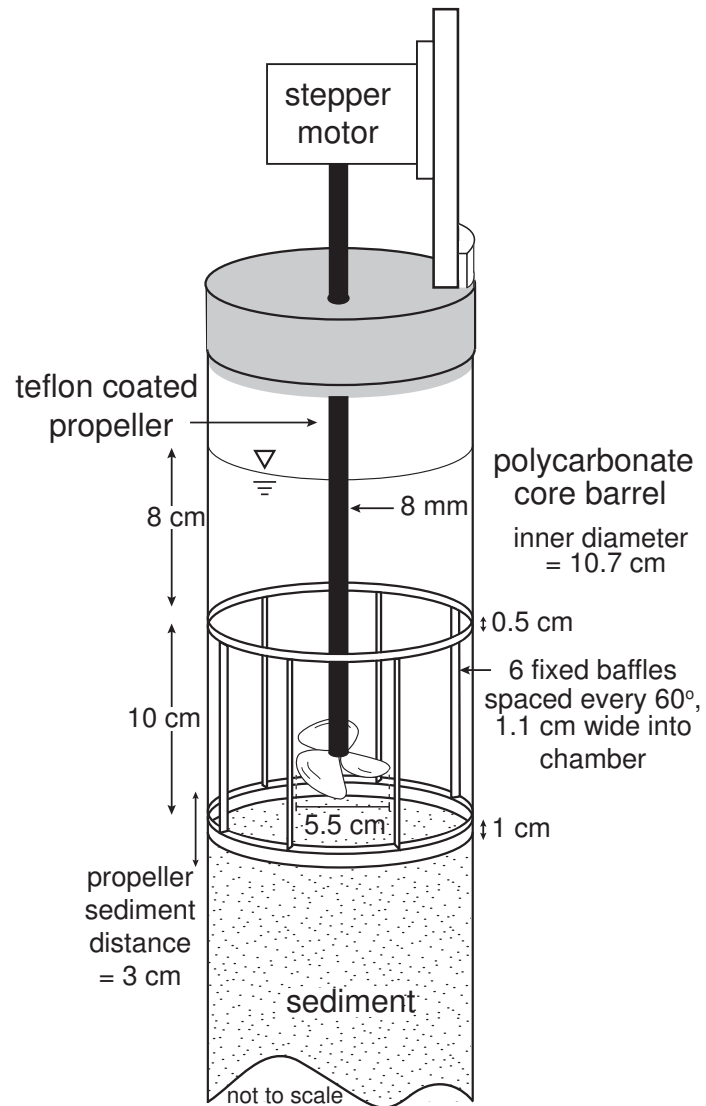


Figure S-1: The modified EROMES erosion chamber showing the experimental geometry [1, 2]. The design for EROMES was provided by Dr Rolf Reithmüller of GKSS, Germany. Drawing by M. Sulanowska.

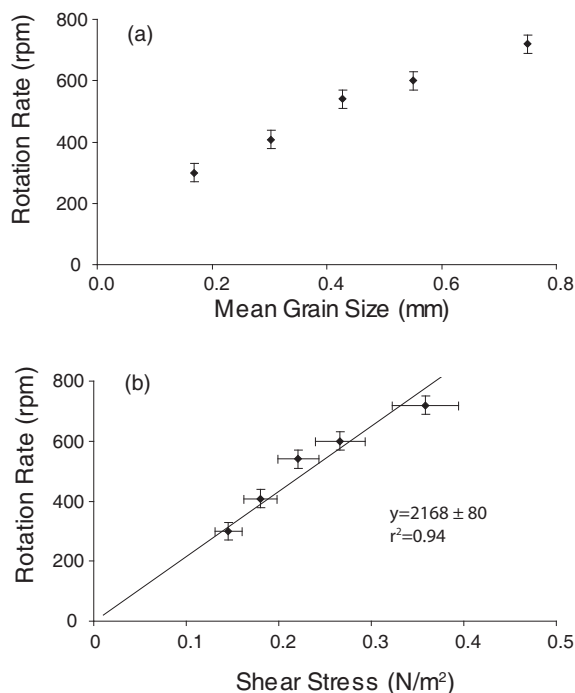


Figure S-2: Erosion chamber calibration curves. (a) Rotation rate at which grains were first held in motion. (b) Shear stress calibration calculated from the Shield's curve for each grain size.

a 5% nitric acid solution containing 0.5 ppb In internal standard solution. A 5% nitric acid matrix external calibration as well as standard additions of a multi-element standard (Alfa Aesar) to selected samples were used to quantify the sample concentrations.

Acid volatile sulfide was determined by a method adapted from Allen [6]. Massachusetts Bay sediment were stored at -40°C for two years prior to AVS analysis. Hingham Bay sediments were stored at -40°C under a nitrogen atmosphere in mylar gas tight bags for 1 year prior to AVS analysis. The H<sub>2</sub>S generated by the method of Allen was trapped in 50 mls of 2.6 % zinc acetate in 1.5 M NaOH and the sulfide concentration determined by the method of Cline [7]. Allen [6] found that frozen sediments stored for 5 months gave values between 80 -90 % of the initial AVS value. These samples have been stored for longer durations but at colder temperatures so it is likely that the AVS values reported do underestimate the initial AVS concentrations. Deeper samples from the MB core have AVS concentrations up to 3 mmol/kg. Samples preserved for the same length of time do have

Table S-1: Sampling Dates and Core Inventory for Hingham Bay

Date	Core Number	Surface Sampling Resolution	Sampling Atmosphere	Analyte
Jan-02	Core 1	3 mm	nitrogen	Porewaters, solid phase
	Core 2	3 mm	nitrogen	Porewaters
	Core 3	2 mm	air	Porosity
Jul-02	Core 1	3 mm	nitrogen	Porewaters
	Core 2	3 mm	nitrogen	Porewaters, solid phase
	Core 3	2 mm	air	Porosity
Sep-02	Core 1	3 mm	nitrogen	Porewaters, solid phase
	Core 2	3 mm	nitrogen	Porewaters
	Core 3	2 mm	air	Porosity
Oct-03	Core 1	3 mm	nitrogen	Porewaters
	Core 2	2 mm	air	Porosity
	Core 3	5 mm	air	Solid phase, porosity
	Core 4			Erosion Experiment
Jun-04	Core 1	3 mm	nitrogen	Porewaters, AVS
	Core 2	3 mm	nitrogen	Porewaters, solid phase
	Core 3	5 mm	air	solid phase, porosity
	Core 4	2 mm	air	Porosity
	Core 5			Erosion Experiment

measurable AVS, indicating that the low levels of AVS in the surface samples of the MB site is due to the geochemical profile in the sediments, rather than a preservation artifact.

Porosity was determined gravimetrically by drying the sediments to a constant weight in a 60°C oven and assuming a grain density of 2.65 g ml<sup>-1</sup> [8].

Acidified porewater samples were analyzed for iron with a Hitachi graphite furnace atomic absorption spectrophotometer (GFAAS), quantified with a matrix matched 5 point external calibration. The detection limit was 2  $\mu\text{mol/L}$ . Porewater sulfide was determined by the method of Cline [7]. The detection limit was 1  $\mu\text{mol/L}$ .

Table S-2: Sampling Dates and Core Inventory for Massachusetts Bay

Date	Core Number	Surface Sampling Resolution	Sampling Atmosphere	Analyte
Feb-02	Core 1	3 mm	nitrogen	Porewaters
	Core 2	3 mm	nitrogen	Porewaters
	Core 3	3 mm	nitrogen	Porewaters, solid phase
	Core 4	2 mm	air	Porosity
May-02	Core 1	3 mm	nitrogen	Porewaters
	Core 2	3 mm	nitrogen	Porewaters
	Core 3	3 mm	nitrogen	Porewaters, solid phase
	Core 4	2 mm	air	Porosity
Oct-02	Core 1	3 mm	nitrogen	Porewaters
	Core 2	3 mm	nitrogen	Porewaters, solid phase
	Core 3	2 mm	air	Porosity
Mar-03	Core 1	5 mm	air	solid phase
Jun-03	Core 1	5 mm	air	solid phase
Sept-03	Core 1	3 mm	nitrogen	Porewater nutrients, AVS
	Core 2	3 mm	nitrogen	Porewaters, solid phase
	Core 3	5 mm	air	Solid phase
	Core 4			Erosion Experiment

## Hydrodynamic Modeling of Shear Stresses

To determine the temporal variation of bottom shear stresses at the Hingham Bay site a modeling and statistical approach was used. Hourly wind data collected by the National Data Buoy Center (NOAA), buoy number 44013 was available for a 19.4-year time period, August 1984 to December 2003. This buoy is located in Massachusetts Bay, 20.6 km northeast of the Hingham Bay site. Wind stresses were calculated from the formulation of Large and Pond [9]. Tidal currents for the 19.4 year period were predicted using tidal constituents for the Hingham Bay site. The constituents were determined by running a 100-m horizontal resolution depth-averaged tidal model TRIM [10] driven by the 5 dominant NOAA tidal constituents for Boston Harbor (O1, K1, N2, M2, S2). The tidal constituents for the HB site were determined using the program of Pawlowicz et al. [11] and a 19.4-year period prediction created from the tidal constituents.

The wind-driven currents for the 19.4-year period were predicted using a transfer function between wind and current determined from the hydrodynamic model for each 10 degrees of wind angle. A constant transfer factor for each wind angle was determined, and the input series of wind-stress angle and magnitude converted into current angle and magnitude. Wave driven currents for the 19.4-year period were determined by calculating the wave height and period using the shallow water, fetch limited wave formula [12]. The bottom orbital velocities were calculated using the explicit method detailed in Dean and Dalrymple [13].

For waves and currents exceeding  $0.01 \text{ m s}^{-1}$ , the Grant and Madsen [14] wave-current interaction formula was used to calculate combined shear stress. The depth-averaged currents (tide + wind-driven) were converted to 1 m above bottom using the model drag coefficient ( $c_d=0.003$ ). A constant physical bottom roughness of  $k_b=0.0001 \text{ m}$  was assumed.

## Sediment Results

Table S-3: Chemical Characteristics of Surface Sediments Collected with the Erosion Experiments Cores

Sampling Date	Depth (mm)	Surface Solid Phase Content (mmol/kg dry weight)						
		Fe	Mn	Ag	Pb	Cu	AVS	%OC
Hingham Bay								
Sept. 2003	0-5	755	12.3	0.023	0.34	1.04	n.a	2.7
June 2004	0-3	812	11.9	0.027	0.37	1.03	1.8	3.3
June 2004	3-6	802	11.6	0.024	0.37	1.00	3.9*	3.4
Massachusetts Bay								
Oct. 2003	0-5	479	9.1	0.006	0.3	0.49	n.d	1.8

\* 6-9 mm sample  
n.d. - not detected  
n.a. - not analyzed

Table S-4: Porosity Profiles for each Sampling Site

Depth (mm)	MB October-02	MB February-2004	MB May-04	HB October-03	HB June-04
0-2	0.86	0.88	0.80	0.88	0.92
2-4	0.85	0.90	0.71	0.84	0.92
4-6	0.85	0.88	0.68	0.82	0.9
6-8	0.84	0.84	0.70	0.82	0.89
8-10	0.83	0.88	0.69	0.84	0.89

Table S-5: Characteristics of Overlying Water used in Erosion Experiments

	Salinity (ppt)	Oxygen (mg/L)	Temp (°C)
HB Oct 03	31.5	235	13
HB June 04	31	280	14
MB Sept 03	32	234	13



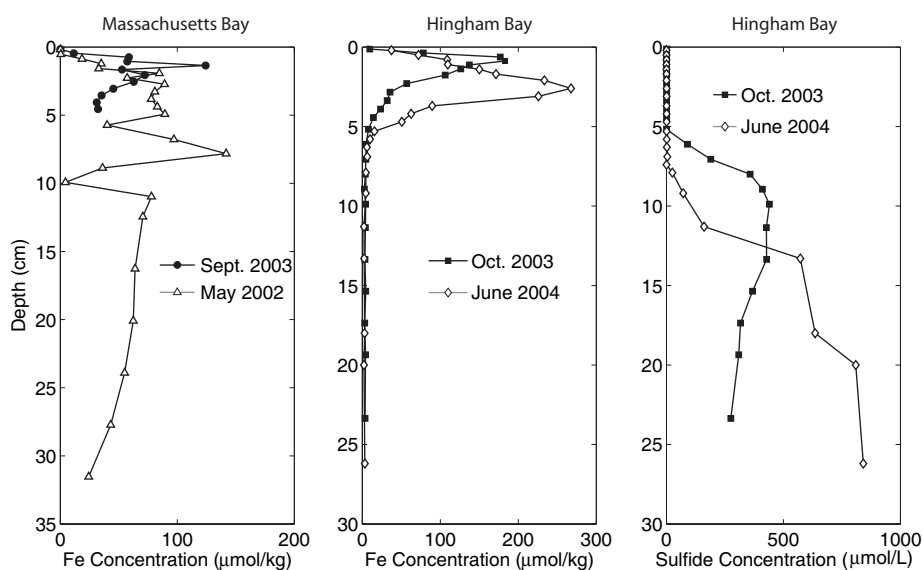


Figure S-3: Iron and Sulfide porewater profiles for Hingham Bay and Massachusetts Bay collected at the same time as each erosion experiment. An additional MB profile from May 2002 is also shown. Sulfide was not detected in the MB cores.

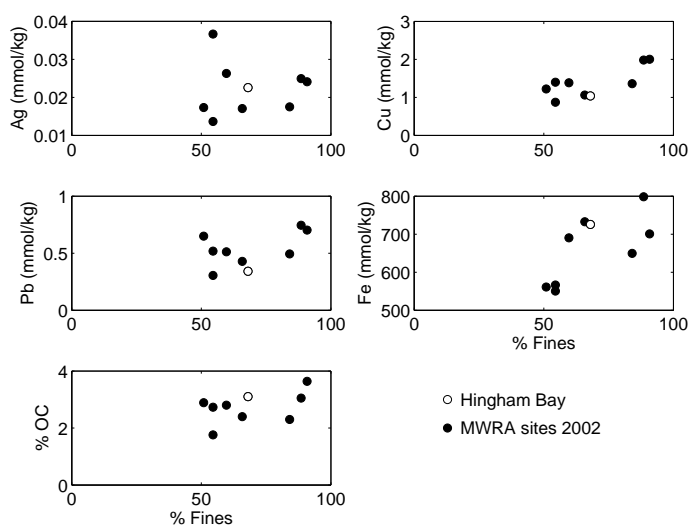


Figure S-4: Surface solid phase metal concentrations measured in 2002 by Lefkovitz et al. [15] for 8 other fine-grained sites within Boston Harbor. The Hingham Bay surface concentrations given in Table 1 are also shown.

## References

- [1] Tolhurst, T.; Riethmuller, R.; Paterson, D. In situ versus laboratory analysis of sediment stability from intertidal mudflats. *Cont. Shelf Res.* **2000**, *20*, 1317-1334.
- [2] Andersen, T.; Jensen, K.; Lund-Hansen, L.; Mouritsen, K.; Pejrup, M. Enhanced erodibility of fine-grained marine sediments by *Hydrobia ulvae*. *J. Sea Res.* **2002**, *48*, 51-58.
- [3] Ravens, T. *Sediment Resuspension in Boston Harbor*, Ph.D. Thesis, Massachusetts Institute of Technology, 1997.
- [4] Soulsby, R.; Whitehouse, R. Threshold of sediment motion in coastal environments. In *Pacific Coasts and Ports '97. Proceedings*, Vol. 1; University of Canterbury, New Zealand, 1997.
- [5] Briggs, P.; Meier, A. *The determination of forty-two elements in geological materials by inductively coupled mass spectrometry*, USGS Open File Report 1999-166, **1999**.
- [6] Allen, H.; Fu, G.; Deng, B. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* **1993**, *12*, 1441-1453.
- [7] Cline, J. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* **1969**, *14*, 454-458.
- [8] Manheim, F.; Dwight, L.; Belastock, R. Porosity, density, grain density and related physical properties of sediments from the Red Sea drill cores. In *Initial Report Deep Sea Drilling Program*; Whitmarsh, R.; Waser, O.; Ross, D., Eds.; U.S. Govt. Printing Office: Washington, D.C., 1974.
- [9] Large, W.; Pond, S. Open ocean momentum flux measurements in moderate to strong wind. *J. Phys. Oceanogr.* **1981**, *11*, 324-336.

- [10] Signell, R.; Butman, B. Modeling tidal exchange and dispersion in Boston Harbor. *J. Geophys. Res.-Oceans* **1992**, *97*, 15591-15606.
- [11] Pawlowicz, R.; Beardsley, B. B.; Lentz, S. Classical tidal harmonic analysis including error estimates in MATLAB using T\_TIDE. *Comput. Geosci.* **2002**, *28*, 929-937.
- [12] U.S. Army Corps of Engineers, Coastal Engineering Research Center, Vicksburg, MS "Shore Protection Manual", 1984.
- [13] Dean, R.; Dalrymple, R. *Water wave mechanics for engineers and scientists*; World Scientific: Teaneck, NJ, 1991.
- [14] Grant, W.; Madsen, O. Combined wave and current interaction with a rough bottom. *J. Geophys. Res.* **1979**, *84*, 1797-1808.
- [15] Lefkovitz, L.; Wisneski, C.; Hunt, C. *Trends In Sediment Contaminant Concentrations In Northern Dorchester Bay And Other Boston Harbor Stations, 1990-2002*, Technical Report 2005-01, Massachusetts Water Resources Authority, **2006**.