Project Report (3-15-2025)

TITLE OF CONTRACT No. 066: Resuspension of contaminants in the Matagorda Bay due to storms, ship traffic, and dredging activities

Jack Lloyd, Zhanfei Liu and Jesscia Dutton

Jack Lloyd is a PhD student who works in Liu Lab of UTMSI, and currently working on this project, but currently being funded by an NSF Fellowship.

Project Summary

Coastal sediments are often the final recipient spots for contaminants due to human activities, such as microplastics, organic contaminants and heavy metals. Sediments are often resuspended due to strong winds, storms, and hurricanes, together with direct disturbances such as shipping activities and dredging. While the levels of contaminants in sediments have often been well determined, it remains unclear how sediment resuspension releases or redistributes the contaminants from sediments to the overlying water. To address this, Drs. Liu, Lu and Ramon will collect sediment cores, simulate sediment resuspension in laboratory, and quantify the amount of contaminants released into the water after the resuspension. The contaminants to be measured include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals. The overall goal is to address a simple question: how do storms and hurricanes affect the water quality of Matagorda Bay?

Instrument Acquisition and Installation

A key piece of instrument for this project is an adapted Gust-Erosion-Microchamber-System (GEMS), and UGEMS is a system assembled by a small company, Green Eyes LLC, the only one available on the market. We purchased the system in June 2024, but due to the constraints of the supply chain and the lack of capital in a small company (couldn't order anything beforehand), the system was not assembled and installed until the end of December 2024 (see the attached picture). Now the system has been installed and the training to use this system has been completed. The next step is to conduct the QA/QC of this system based on the outline (the next section).

QA/QC Outline

Sampling

1. Collect sediment cores from 10 stations in Matagorda Bay using UGEMS tubes. Five stations will be located along the Matagorda Bay ship channel, while the other five stations are evenly distributed to cover the whole Matagorda Bay. At each station, a total of 12 cores with a dimension of ca. 70 cm in length and 10 cm in inner diameter will be collected, sealed, and brought back to Liu lab at UTMSI for the subsequent simulation experiment. Among the 12 cores, 10 will be used to quantify the release of contaminants after sediment resuspension, with 5 different treatments representing 5 different disturbance scenarios with duplication, and a separate pair of 2 samples will be used to measure the erodibility of the sediment.
2. Collect surface water samples in 4 L amber glass bottles (this will be used to enter the erosion chamber). (Dickhudt et al., 2011)
    a. At least 4.5 L per site need to be collected for contaminant analyses
    b. We need at least 5 gallons in total, or ~ 19 L, per Vince.

Lab simulation of sediment resuspension

1. The simulation of sediment disturbance will be achieved in a UGEMS gust erosion microcosm system (Briggs et al., 2015; Dickhudt et al., 2011). Utilizing a circular extruder matching the inside diameter of the core tube, the sediment in the core will be gently pushed upward from below until its surface is ca. 30 cm below the revolving disk, with water collected from the same location filling the space between the sediment surface and the microcosm disk, if necessary. With the rotating disk at the top of the core, a circulation pattern is produced and will apply a nearly uniform shear stress over the sediment-water interface (Briggs et al., 2015; Dickhudt et al., 2011).
2. There will be 5 different disturbance scenarios (4 different shear stresses and one strong agitation). The shear stress will be set to be 0 Pa (not rotating), 0.05 Pa, 0.3 Pa, and 0.6 Pa, representing the resuspension brought by a series of light winds. In addition to the normal condition, a stronger agitation of the sediment will be achieved through vigorous shaking of the sampling core on a shaking table (C2 Platform Shaker; New Brunswick Scientific) with an RPM of 140, and a complete disturbance of the sediment-water interface. This represents the scenario of extremely strong storms (e.g., hurricanes) or the effect of large cargo ship/oil tanker movements (e.g., Bu et al., 2020).
3. The perturbation of the sediment will last ca. 20 min, following previous studies (Briggs et al., 2015; Dickhudt et al., 2011; Feng et al., 2007; Tsai and Lick, 1986).
4. A rest time of ca. 20 min to let the resuspended coarse sediment particles settle down before the subsamples of overlying water and sediments are taken.
5. A total volume of 450 mL overlying water (may include suspended very fine minerals and organic matter) will be collected for analyses of chemicals, including PAHs, PCBs, Hg, and other trace elements (e.g., Ag, Al, As, Cd, Co, Cu, Pb, Se, U, Zn).
6. The top 20 cm of the sediment will also be collected for determining the levels of contaminants (e.g., PAHs and Hg). Samples collected from the controlled group (i.e., no rotation) will represent the background level or control.

Measurement of sediment erodibility

1. Two cores from each site will be used to quantify the erodibility of Matagorda Bay sediment.
2. The setup for erodibility follows the in-lab simulation described above, except that a series of 7 different shear stresses will be applied over a course of 2.5 h. During the first 30 min of the experiment, a shear stress of 0.01 Pa will be applied to flush the system, and the stress will increase to 0.05, 0.1, 0.2, 0.3, 0.45 Pa at 20 min intervals, until a final stress of 0.6 Pa is achieved.
3. Different from the resuspension simulation, a stream of water collected from the field site will be pumped into the core-cosm. The effluents containing the eroded material will be passed through the flow cell of a connected turbidimeter, which records the concentration in NTU unit (Dickhudt et al., 2011; Sanford, 2006).
4. The effluents from each shear stress step will be collected and then filtered onto a 0.7 μm glass-fiber filter to calibrate the turbidimeters and to determine the total mass of sediment eroded from both cores.
5. The measurements of eroded mass (m) from the bed as a function of time (t) will be analyzed using the erosion rate formulations of Sanford and Maa (2001) and Sanford (2006) as implemented by Dickhudt et al. (2011).

Extraction of contaminants in overlying water and sediment.

1. Specifically, one aliquot of collected overlying water (10 mL) will be preserved in an acid-cleaned 20 mL plastic bottle, and then sent to Dutton lab for Hg analysis. These samples will be analyzed within 28 days after collection. Total Hg of the overlying water after disturbance from all 10 stations will be determined. The speciation of Hg will be analyzed for samples from stations 1 - 5 to acquire a better understanding of the dynamic of Hg in the ship channel region due to resuspension.
2. A second aliquot of overlying water (30 mL) will be filtered through a syringe filter into a pre-clean polycarbonate bottle for the analyses of other trace elements. All syringes, syringe filters, and bottles used for the trace metal analysis will be pre-cleaned with trace metal grade HNO3 and rinsed with nanopure grade water.
3. A third aliquot of 200 mL will be extracted via solid phase extraction (SPE) using an Oasis HLB cartridge for PCBs (e.g., Bassignani, 2011; Stubleski et al., 2018). Previous works have demonstrated an overall recovery rate of ca. 70% for HLB cartridges.
4. The leftover samples (200 mL) will be extracted via SPE using a Biotage total petroleum hydrocarbons cartridge (ISOLUTE® TPH) for PAHs analysis. Our previous results have shown that the recovery rate of PAHs is over 87% based on deuterium labeled internal standard (unpublished data in Liu Lab).
5. The extraction of PAHs and PCBs from sediment will follow the published procedure in Liu Lab (Wang et al., 2012). Briefly, 5 g of freeze-dried sediments, spiked with isotopically labeled PAHs (phenanthrene-d10) and PCBs (PCB-204), are extracted with accelerated solvent extraction (ASE300 from DIONEX, USA) using a mixture of acetone and dichloromethane (1:1 v/v). The extraction cells are heated to 100 °C. The static time is set to be 5 min, with a flush volume of 60%, and a purge time of 90 s. The final volume

of the extract is approximately 30 – 40 mL, which is further concentrated to about 2 mL by a gentle blow of N2 gas. The final sample will be preserved at -20 °C until further analysis on GC-MS. The recovery rate of sediment extraction is generally over 85%.

Analysis of contaminants in overlying water and sediment.

1. Water and sediment samples will be analyzed for Hg using a Direct Mercury Analyzer (DMA-80; Milestone Inc., Shelton, CT) in Dutton Lab. The DMA utilizes thermal combustion, gold amalgamation, and atomic absorption spectroscopy as described in EPA Method 7473 (US EPA, 2007). The DMA will be calibrated as needed using certified reference materials (CRMs) from the National Institute of Standards and Technology [NIST 1566b, oyster tissue (0.0371 μg/g Hg)], National Research Council Canada [NRCC; TORT-3, lobster hepatopancreas (0.292 μg/g Hg)], and European Reference Materials [ERM-CE464, tuna (5.24 μg/g Hg)]. One round of quality control, including a blank (empty quartz boat), CRM [MESS-4, marine sediment (0.08 μg/g Hg), PACS-3, marine sediment (2.98 μg/g Hg); and DORM-4 fish protein (0.412 μg/g Hg); all from the NRCC], and duplicate sample will be included with every 10 samples analyzed. To pass quality control, the blank should have a Hg concentration ≤ 0.0001 μg/g, the recovery of the CRMs should be between 90% and 110%, and the relative percent difference between duplicate samples be ≤ 10%.All Hg analysis will occur in year 1.
2. The concentration of other trace elements in sediment (0.25 g) and water samples (0.25g) will also be determined in Dutton Lab. Water analysis will occur during year 1 and sediment analysis during year 2.
3. Concentrations of 16 EPA priority PAHs and 7 PCB congeners will be quantified, namely naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k,j]fluoranthene (BkF), benzo [a]pyrene (BaP), indeno[1-3]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP), PCB-28, PCB-52, PCB-101, PCB153, PCB-138, PCB-180 and PCB-209. Both PAHs and PCBs will be analyzed by a gas chromatography mass spectrometer (GC-MS; Shimadzu, GCMS-QP2020) equipped with an RXi-1MS capillary column (20 m × 0.18 mm i.d., film thickness 0.18 μm; Wang et al., 2014; Jiang et al., 2021) in Liu Lab.
4. The measurement of PAHs and PCBs will follow our published works (Jiang et al., 2021). Briefly, for PAHs analysis, 1 μL of the solution will be injected with a split ratio of 1/20. The oven temperature is held at 60 °C for 1 min, increased to 240 °C at a rate of 10 °C min-1, and then increased to 280 °C at a rate of 4 °C/min and held for 31 min. For PCBs, 2 μL of the solution will be injected with a split ratio of 1/10. The oven temperature is increased from 50 °C to 320 °C at a rate of 5 °C/min, and held for 10 min. The PAH and PCB analysis will be performed mostly during year 2 of the project.

The next steps

We expect to finish the QA/QC before the end of May. Then we will have cruises to collect sediment samples in Matagorda Bay. In other words, we plan to conduct the field work and the experiment during this summer in 2025. Works Cited

Briggs, Kevin B., et al. "Biogenic effects on cohesive sediment erodibility resulting from recurring seasonal hypoxia on the Louisiana shelf." *Continental Shelf Research* 93 (2015): 17-26.

Butman, Bradford, et al. "Investigating the importance of sediment resuspension in *Alexandrium fundyense* cyst population dynamics in the Gulf of Maine." *Deep Sea Research Part II: Topical Studies in Oceanography* 103 (2014): 79-95.

Dickhudt, Patrick J., Carl T. Friedrichs, and Lawrence P. Sanford. "Mud matrix solids fraction and bed erodibility in the York River estuary, USA, and other muddy environments." *Continental Shelf Research* 31.10 (2011): S3-S13.

Valentine, Kendall, and Giulio Mariotti. "Does eutrophication affect the ability of biofilms to stabilize muddy sediments?." *Estuarine, Coastal and Shelf Science* 232 (2020): 106490.