Electronic Supporting Information

Harnessing Salinity Gradient Energy in Coastal Stormwater Runoff to Reduce Pathogen Loading

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Mixing Entropy of Stormwater and Seawater

The amount of salinity gradient energy (ΔG_{mix}) that is available in the mixing of ocean water and stormwater is calculated by:[1]

$$\Delta G_{mix} = 2RT[V_{St}C_{St}ln\frac{C_{St}}{C_M} + V_O C_O ln\frac{C_O}{C_M}]$$

where C_{St} is the NaCl concentration (mol m^{-3}) in the stormwater (e.g., 5 mM is similar to the average salinity found in stormwater monitoring studies),[2] C_O the NaCl concentration (mol m^{-3}) in the ocean (e.g., 0.6 M), V_{St} the volume of stormwater (m^3), V_O the volume of ocean water (m^3), R the universal gas constant (8.314 J mol^{-1} K^{-1}), and T the absolute temperature in Kelvin. C_M is the NaCl concentration (mol m^{-3}) after complete mixing of stormwater and ocean water:

$$C_M = \frac{V_{St}C_{St} + V_O C_O}{V_O + V_{St}}$$

Assuming that $V_O >> V_{St}$, the maximum available ΔG_{mix} approaches ~0.79 kWh m^{-3} for the synthetic stormwater and seawater as the volume ratio approaches infinity. For the real stormwater and seawater, salinities were used to approximate NaCl concentration. An average salinity of 0.37 ppt and 33.4 ppt was found in the stormwater and seawater, respectively. The maximum available ΔG_{mix} then approaches ~0.75 kWh m^{-3} as the volume ratio approaches infinity, or 3780 J for the 1.4 L of inlet stormwater.

Electrode Fabrication

Preparation of Prussian Blue (PB) Electrode

We prepared Prussian Blue powder with a solution based reaction:

$$Na_3[Fe(CN)_6] + FeCl_3 \rightarrow 3NaCl + Fe[Fe(CN)_6]$$

0.5 M sodium ferricyanide solution (Sigma-Aldrich) was first mixed with 0.5 M ferric chloride (Alfa Aesar) in a hydrochloric acid (Sigma) solution at pH=2. After 72 h of mixing, the sample was centrifuged and washed three times with deionized water, then dried in a vacuum oven. The PB powder was then coated on plain carbon cloth (275 μm thickness, FuelCellEarth LLC) with a slurry-coating method. The slurry was prepared by mixing dry PB powder (85% wt.) with Super-P (TIMCAL, 8% wt.) and PVDF (MTI Inc., 7% wt.). We then added N-methyl pirrolidone (NMP, Sigma) to the mixture as solvent, and stirred the ink overnight before coating the carbon cloth and drying in a vacuum oven for 24 h. To prevent attrition of the PB particles on the electrode, a Na^+ permeable polyvinyl alcohol/sulfosuccinic acid (PVA/SSA) coating was also used, and prepared according to the literature.[3,4] A solution of PVA (99+% hydrolyzed, average molecular wt. 130,000, Sigma-Aldrich, 10% wt.), SSA (Sigma-Aldrich, 30% wt.) and DI water

(60% wt.) was stirred vigorously for 24 hours, then coated on the PB electrode with a scalpel blade. The electrode was then placed in an oven at 60 ºC for one hour, 130 ºC for another hour, and cooled to room temperature prior to using. PB mass loading was varied (a range of 3 to 21 mg cm^{-2}) for the 3 cm × 3 cm electrodes to determine the impact of mass loading on power production, mass loading was fixed at 7 mg cm^{-2} for the 25 cm × 25 cm electrodes.

Preparation of Polypyrrole (PPy) Electrode

We prepared the PPy electrode by electrochemically polymerizing PPy on plain carbon cloth (275 μm thickness, FuelCellEarth LLC) with a 0.1 M pyrrole (Sigma-Aldrich) solution in the presence of NaCl (1 M). An anodic current of 1 mA/cm^2 was applied for polymerization of PPy. The PPy electrode was then electrochemically reduced with a potentiostat (Biologic SP-50) in a 0.6 M NaCl solution to a potential of 0.2 V vs Ag/AgCl (3.5 M KCl). Electropolymerization charge passed was varied (a range of 7.2 to 21.6 C cm^{-2}) for the 3 cm × 3 cm electrodes to determine the impact of PPy mass loading on power production, charge passed was fixed at 14.4 C cm^{-2} for the 25 cm × 25 cm electrodes.

Synthetic and Real Waters

Real water characterization

On-site measurements of flowrate, turbidity, salinity, and temperature were taken daily for the duration of the in-ocean MEB bench-pilot experiments. All measurements were taken twice (n=2). Flowrate was measured by measuring the time by stopwatch to fill a 2.0 L graduated cylinder. Flowrate did not fluctuate significantly during the course of the experiments (Figure S1) and was thus measured just once per day. This was due to zero precipitation during the

period Feb 19 to Feb 21, 2019 for Half Moon Bay, CA (usclimatedata.com). Total precipitation between Feb 13, 2019 and Feb 18, 2019 totaled 2.47 inches (usclimatedata.com).

50 mL samples were taken in clean sterile containers from the stormwater outfall (after passing through a 5 μm UV-LED pre-filter) and immediately analyzed for salinity (factory calibrated by conductivity, SevenGo Duo, Mettler-Toledo), temperature (SevenGo Duo, Mettler-Toledo) and turbidity (DRT-15CE, HF Scientific). For enumeration of *Escherichia coli* concentration in source, treated, and control waters, the following methods were used: Source: 500 mL samples were taken in clean sterile containers from the stormwater outfall (after passing through a 5 μm factory-supplied pre-filter); Treated: 500 mL samples were taken in clean sterile containers after passing through the UV-LED module (but before entering the MEB); Control: 500 mL samples were taken in clean sterile containers after passing through the UV-LED module (but before entering the MEB), but with the UV-LED turned off. Enumeration samples were immediately stored in an insulated 4°C cooler. The samples were analyzed in the lab approximately 1 hr after collection by using a colorimetric-liquid-defined substrate assay (Colilert, IDEXX Laboratories). Samples were first decimally diluted and multiple dilutions were assayed. All dilutions that yielded measurements within the assay range of quantification were quantified using an MPN table provided by IDEXX. The assay detection limit was 10 most probable number (MPN) 100 mL^{-1}. Only *E.coli* was enumerated.

MEB Construction and Operation

Single-cell MEB

In the single-cell lab-scale system, the 3 cm × 3 cm MEB electrodes were placed in an acrylic plate-shape chamber with the dimension of 3 cm × 3 cm × 0.3 cm. The volume of the

chamber was 1.5 mL after embedding the PB electrode and the PPy electrode (Figure S2). A thin plastic mesh separated the electrodes, and a single titanium wire was used to connect the electrode to the external circuit in the cell. The electrode ends were connected to a variable resistor (5 – 5000 Ω), a potentiostat (Bio-logic SP-50) was used to generate power curves by measuring the voltage and calculating the power across variable resistances. The cell was alternately flushed with synthetic stormwater (0.005 M NaCl) and seawater (0.6 M NaCl), power was measured directly after the saline stream flush.

In-ocean bench-pilot

In the bench-pilot system, 32 pairs of 25 cm × 25 cm PB and PPy electrode cells were stacked in a waterproof acrylic housing, each was hydraulically separated to prevent short-circuiting and each cell had a thin plastic mesh separator between the anode and cathode. Four titanium wires (spaced 5 cm apart) were used to connect the electrodes to the external circuit. The total internal liquid volume was 1.4 L. A single 25 cm × 25 cm cell pair was connected to a fixed resistor (5 Ω) to evaluate the impact of cycle duration on power production and energy capture in the lab using synthetic stormwater (0.005 M NaCl) and seawater (0.6 M NaCl). For in-ocean testing, cells were configured in four groups of cells in series, each with eight cells in parallel (Figure S3). The MEB voltage output was boosted to ~3.8 V with a bootstrap converter (VB0410, TXL Inc.) to store the captured SGE in a lithium ion battery (Panasonic NCR18650B). A manual switch was used to change polarity between stormwater and seawater flushes as the voltages were opposite polarities (Figure S4). For utilizing the SGE stored in the lithium ion battery, a DC-DC buck boost voltage converter (Eboot DSN6009) converted the Li-ion voltage (~3.7 V) to 8.8 V to power the UV-LED module (Eco Purifier, > 20 mJ cm^{-2} at 260-275 nm peak wavelength

using Crystal IS Klaran WD UV-LEDs, Acuvatech Inc.) used to disinfect the inlet stormwater prior to entry into the MEB. The UV-LED module allowed a flowrate of 1.46 L min^{-1}, consuming 7.4 W (measured experimentally). The UV-LED module shuts down if sufficient power is not supplied to the UV-LED. Figure S4 shows a photograph and circuit schematic of the system. An inline 5 μm pre-filter supplied by the manufacturer was used to aid in removing particulate matter.

Operation of the pilot was as follows: i) The MEB unit was placed on the ocean floor 0.3 m underwater (at low tide) in a protected cove and secured with weights and large rocks. The unit was placed in the ocean to avoid consuming energy for pumping ocean water to shore; ii) A tube from the stormwater outfall (approximately 50 m up shore) was run to the underwater MEB to supply the low salinity stormwater until the MEB unit was full (1.4 L). A solenoid valve on a timer was embedded in the acrylic MEB container to control this. Figure S3 shows the bench pilot unit prior to testing and underwater during testing; iii) The stormwater remained in the MEB unit for 6 hours while Na^+ and Cl^- ions migrating out of the intercalation electrodes and into the stormwater (producing power). The output power was run back to shore via waterproof cables, the energy was captured and stored by the power electronics and battery (Figure S4), which supplied power to the adjacent UV-LED. Because of the lag between stormwater flow and energy capture, the first stormwater flush did not power the UV-LED; iv) Air was supplied to the MEB unit (via the inlet hose with the exit solenoid valve open) by a pressurized tank for approximately 5 s to remove the stormwater into the ocean; v) the solenoid valve was left open for six hours to allow migration of seawater into the unit, Na^+ and Cl^- ions migrated into the intercalation electrodes (also producing power); vi) air was supplied to the unit to remove the seawater; vii) the cycle repeated.

Challenges of the pilot operation were significant, which resulted in only 3 days of testing. The first several potential testing sites resulted in significant movement of the unit by waves and tides. Even with the protected cove site we chose, by day 3, waves had washed the unit to shore, and breakage corroded the electronics, resulting in only 3 days of in-ocean testing. We suggest subsequent testing to take place out of water to prevent these challenges, but close to sea level, in order to minimize pumping requirements of seawater to the MEB unit. However, this will require more efficient units to provide sufficient power for the pump.

References

1 J. Veerman, M. Saakes, S. J. Metz and G. J. Harmsen, Reverse electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water, *J. Memb. Sci.*, 2009, **327**, 136–144.

2 P. Göbel, C. Dierkes and W. G. Coldewey, Storm water runoff concentration matrix for urban areas, *J. Contam. Hydrol.*, 2007, **91**, 26–42.

3 D. S. Kim, M. D. Guiver, S. Y. Nam, T. Il Yun, M. Y. Seo, S. J. Kim, H. S. Hwang and J. W. Rhim, Preparation of ion exchange membranes for fuel cell based on crosslinked poly(vinyl alcohol) with poly(styrene sulfonic acid-co-maleic acid), *J. Memb. Sci.*, 2006, **281**, 156–162.

4 Y.-J. Kim and J.-H. Choi, Improvement of desalination efficiency in capacitive deionization using a carbon electrode coated with an ion-exchange polymer, *Water Res.*, 2010, **44**, 990–996.

Supporting Figures

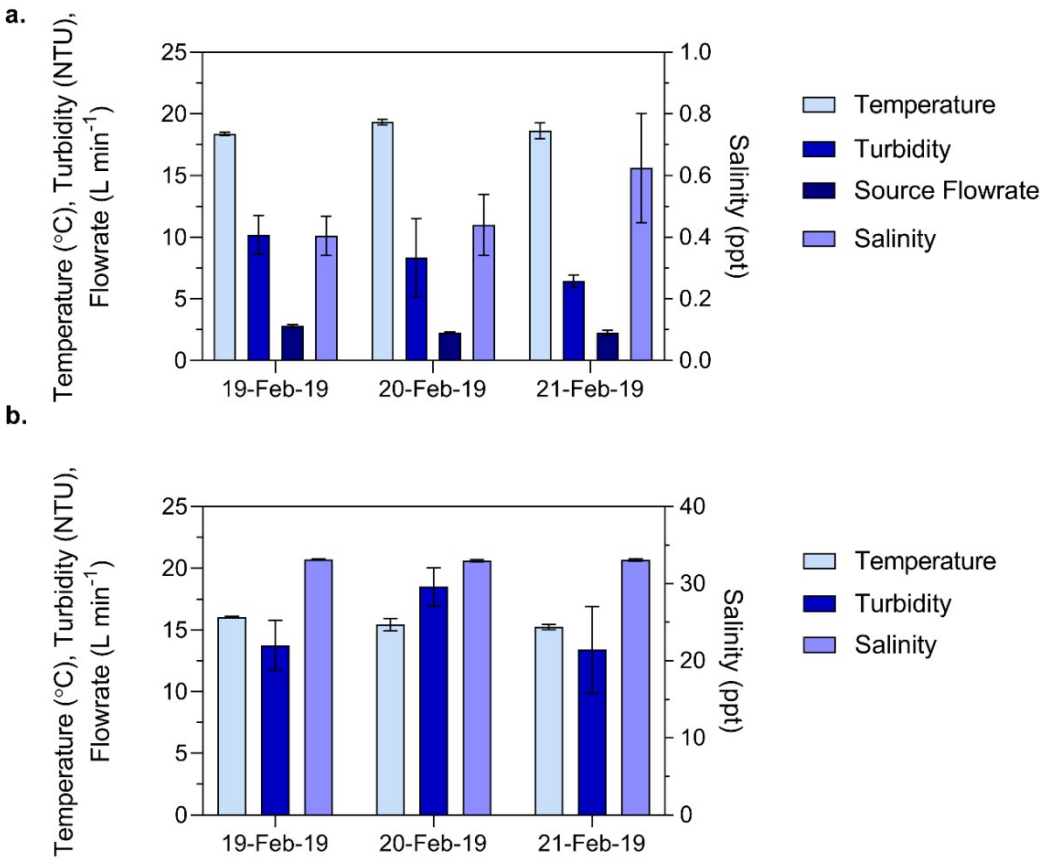


Figure S1 – (a) Temperature, turbidity, flowrate, and salinity of stormwater at source from Feb 19, 2019 to Feb 21, 2019. (b) Temperature, turbidity, and salinity of seawater at in-ocean MEB site. n=2 for all measurements. Bar height represents mean, error bars represent standard deviation.

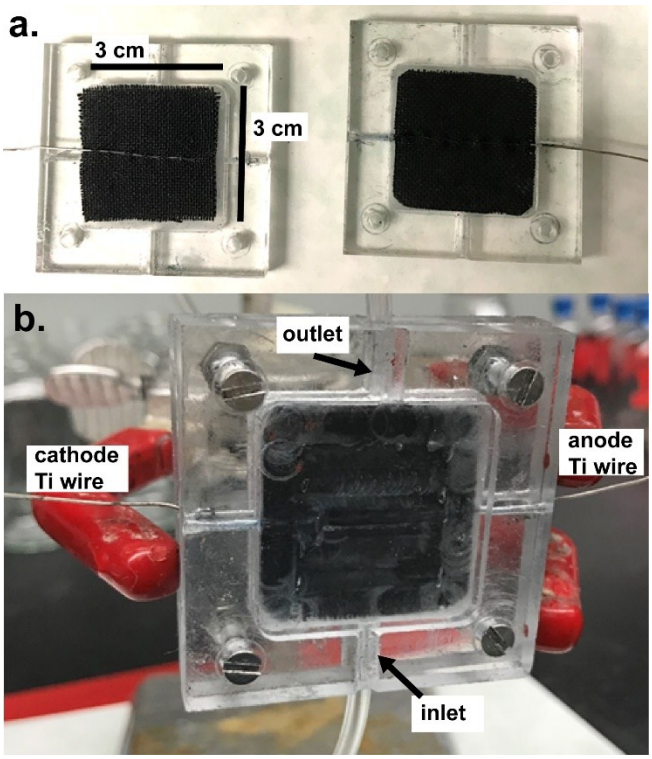


Figure S2. (a) individual 3 cm × 3 cm electrodes, PB (right) and PPy (left) electrodes. (b) 3 cm × 3 cm electrode system assembly.

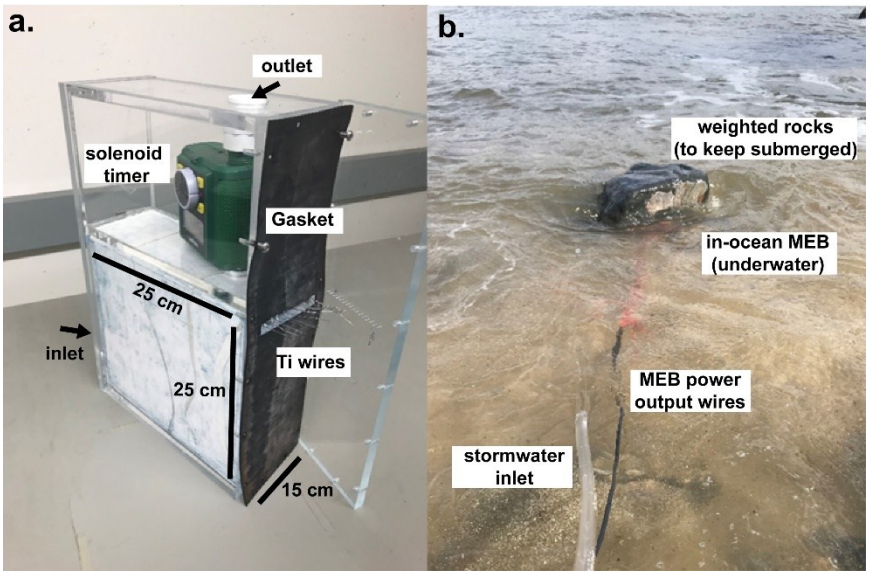


Figure S3. (a) 25 cm × 25 cm bench-pilot MEB in lab, (b) 25 cm × 25 cm bench-pilot MEB operating underwater.

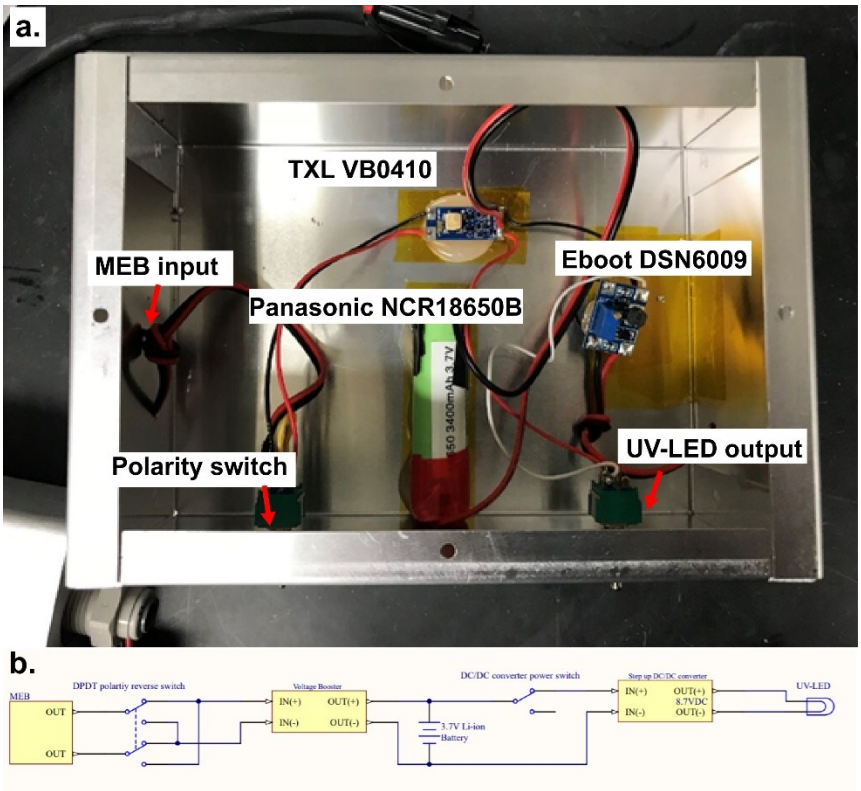


Figure S4. (a) Internal circuitry for power capture and conversion. (b) Power electronics circuitry schematic.

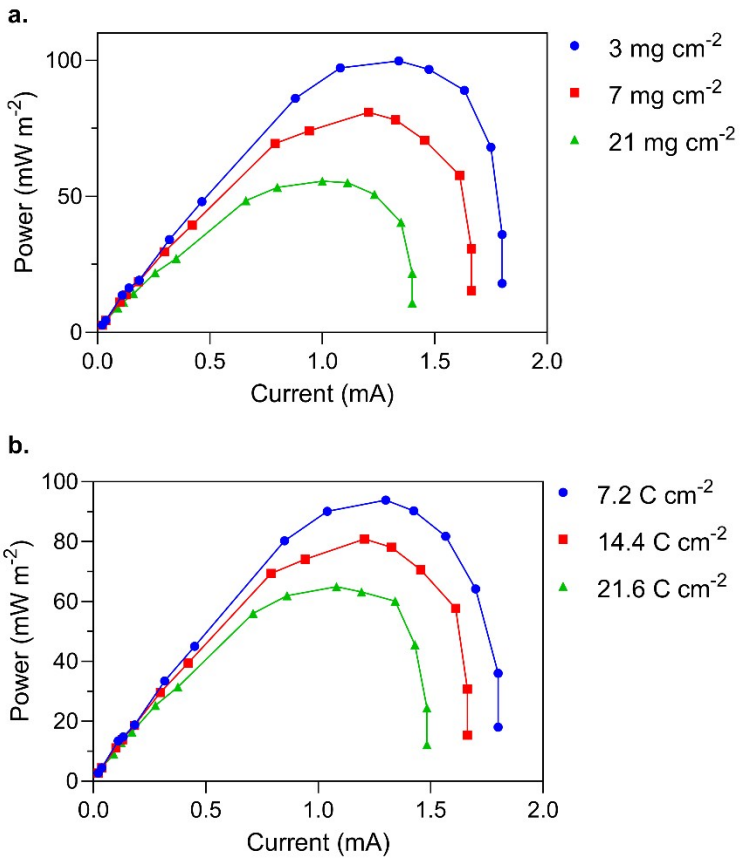
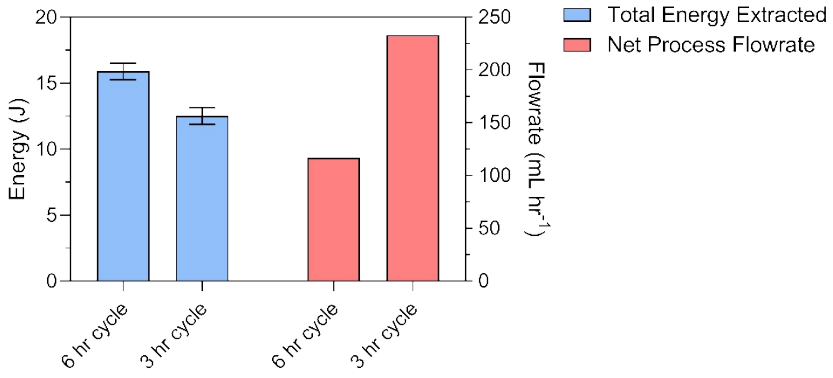


Figure S5. (a) Impact of PB mass loading on power curves, PPy deposition charge of 14.4 C cm^{-2}. (b) Impact of PPy deposition charge on power curves, PB mass loading of 7 mg cm^{-2}. All data for single 3 cm × 3 cm cell.



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180 **Figure S6. Total energy extracted per cycle and net process flowrate for 3 hr and 6 hr cycle**
181 **duration times. Bar height represents mean, error bars represent standard deviations.**

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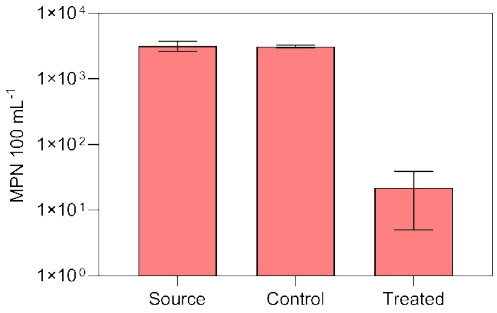

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185 **Figure S7. (c) *E.coli* reduction by UV-LED and control for in-ocean system after 48 hr of**
186 **pilot testing, n=2. Bar height represents mean, error bars represent standard deviations.**

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