Autonomous, retrievable, deep sea microbial fuel cell

Kenneth Richter, Robert George, Jeffrey Kagan, Joshua Richmond
Environmental Assessment and Sustainability
SPAWAR Systems Center, code 71751
San Diego, CA USA
ken.richter@navy.mil

Abstract— **Microbial fuel cells (MFCs) work by providing bacteria in anaerobic sediments with an electron acceptor (anode) that stimulates metabolism of organic matter. The buried anode is connected via control circuitry to a cathode exposed to oxygen in the overlying water. During metabolism, bacteria release hydrogen ions into the sediment and transfer electrons extra-cellularly to the anode, which eventually reduce dissolved oxygen at the cathode, forming water. The open circuit voltage is approximately 0.8 v. The voltage between electrodes is operationally kept at 0.4 v with a potentiastat. The current is chiefly limited by the rate of microbial metabolism at the anode. The Office of Naval Research has encouraged development of microbial fuel cells in the marine environment at a number of academic and naval institutions. Work at SPAWAR, a navy laboratory in San Diego, involves fuel cell design and testing, applications to low power Navy sensors, and studies of important environmental parameters that affect fuel cell performance.**

Earlier work in shallow sediments of San Diego Bay showed that the most important environmental parameters that control fuel cell power output in San Diego Bay were total organic carbon in the sediment and seasonal water temperature. Parameters that we dismissed as unimportant were dissolved oxygen levels, light level, and initial sediment bacterial populations. Parameters whose affect we could not separate were total organic carbon and grain size.

Current MFC work at SPAWAR includes extension of microbial fuel cell tests to the deep sea environment (>=1000 m) and, in parallel, testing microbial fuel cells in the laboratory under deep sea conditions. One question we are asking is whether MFC power output from deep water sediments repressurized and chilled in the laboratory comparable to those measured in situ. If yes, mapping the power potential of deep sea sediments may be made much easier, requiring sediment grabs and lab tests rather than deployment and retrieval of fuel cells. Another question we are asking is whether in situ temperature and total organic carbon in the deep sea sediment can predict MFC power. If yes, then we can make use of the large collection of publicly available, deep sea oceanographic measurements to make these predictions, foregoing expensive work at sea.

In order to meet these goals we are pursuing a field effort to (1) deploy a microbial fuel cell in progressively deeper water, (2) record in situ power and temperature over several weeks, and (3) retrieve the fuel cell along with sediment samples for analysis. We are also pursuing a laboratory effort to (1) build a matching microbial fuel cell in a pressure vessel capable of matching the pressure and temperature of deep water, (2) capable of flushing the fuel cell with oxygenated water under pressure to allow equilibrium power production, and (3) stock the pressure vessel with deep water sediment in order to take measurements analogous to those in the field. The current progress and results from this work at SPAWAR will be presented.

Keywords—component; formatting; style; styling; insert (key words**)**

I. INTRODUCTION

Sediment-based microbial fuel cells (MFCs) are fuel cells powered by the metabolism of organic material by facultative aerobic bacteria living in anaerobic sediments. During metabolism, organic matter is oxidized (electrons are released) and some electron acceptor is reduced (electrons are accepted). These particular bacteria (e.g. *Geobacter and Shewanella* sp.) are capable of taking advantage of a buried electrode, electrically linked to an oxygenated environment as an electron receptor [e.g.1,2]. While the metabolic pathways of these organisms are not well understood [3], the key feature is transport of electrons, released during intra-cellular oxidation of organic matter, to an extra-cellular electron acceptor poised by reduction of oxygen. In parallel to electron transport to oxygen, hydrogen ions are released during metabolism as well, diffuse into the sediment and overlying water column, and combine with reduced oxygen at the cathode to form water.

In a previous report [4] we found that the most important environmental parameters that control fuel cell power output in San Diego Bay were total organic carbon in the sediment and seasonal water temperature. Derived relationships between power and organic carbon, temperature and anode size, along with extensive knowledge of sediment organic carbon and seasonal water temperatures in San Diego Bay, allowed us to develop seasonal contours of power output from a benthic microbial fuel cell. This study examines MFC output in sediments at greater water depth where seasonal temperature changes are more moderate, organic material in the sediment may be more refractory, and increasing pressure with depth may select for barophilic communities [5]. The basic question we are asking is whether in situ temperature, sediment organic carbon and perhaps pressure can be used to predict deep sea MFC power output in a manner similar earlier shallow water studies. If yes, then we can make use of the

large collection of publicly available, deep sea oceanographic measurements to make these predictions, foregoing expensive work at sea.

A deep sea (>1000 m) free vehicle that supports one or more MFCs and returns to the surface via acoustic release is described. The vehicle is designed to capture and return sediment samples (unpressurized) from around the MFC anode, as well as reference sediments not subjected to MFC energy harvesting. A parallel laboratory effort is also presented where in situ pressure and temperature conditions of the deep sea can be mimicked in a flow-through pressure vessel that accommodates a MFC. Sediment returned from the deep sea after retrieval of the free vehicle or from other oceanographic studies of opportunity is used in the laboratory tests. The purpose of the laboratory tests is to determine whether laboratory MFC measurements of deep sea sediments can be used in lieu of difficult in situ measurements, or whether the temporary depressurization and warming of deep water sediments introduces an unacceptable bias to these measurements in the lab. Preliminary data from both efforts is presented.

II. Methods and Approach

A. Deep Sea Free Vehicle

Figure 1 shows a cartoon of the free vehicle which supports one to three MFCs. The MFC electrodes and recording electronics were constructed by Peter Kauffman (Northwest Metasystems, Seattle, WA) and have been described earlier [4]. Measured parameters include: (1) the voltage difference between the anode and cathode (set by the potentiastat at typically 0.385 v), (2) the current flowing between the anode and cathode, and (3) the voltage difference between the anode and a Ag/AgCl reference electrode. The latter measurement is indicative of the redox state of the electrodes. The electrodes and electronics are the same design as used in shallower water studies. A self-recording thermistor (Hobo data logger from Onset Computers, Bourne, MA) is often included in the pressure case. Essentially, three polycarbonate tubes with closing covers are attached to an aluminum cylinder and suspended below a ballast platform. The tubes can support MFC anodes that are forced into the sediment went the vehicle lands on the bottom. Three floatation spheres provide buoyancy to bring the MFCs and partially submerged tubes to the surface when an acoustic release drops the ballast, which remains on the bottom. The tubes have closing covers to retain sediment and are version of those found on a sediment corer (Tim Marrs, Ocean Instruments, San Diego CA), modified to close when the aluminum cylinder separates from the ballast platform (Fig 2). The tubes can return either reference sediment or sediment impacted by the MFC, depending on whether it is outfitted with an anode. The vehicle typically descends with a net weight of 70 kg and ascends with a net buoyancy of 70 kg. Descent and ascent rates are approximately 1 m sec^{-1}. At the surface, a pressure-triggered strobe, GPS and radio transmitter package designed by Kevin Hardy (Global Ocean Design, San Diego, CA) inside one of the floats aids in recovery. Figure 3 shows the vehicle on recovery after a month-long deployment at 1000 m with full sediment tubes.

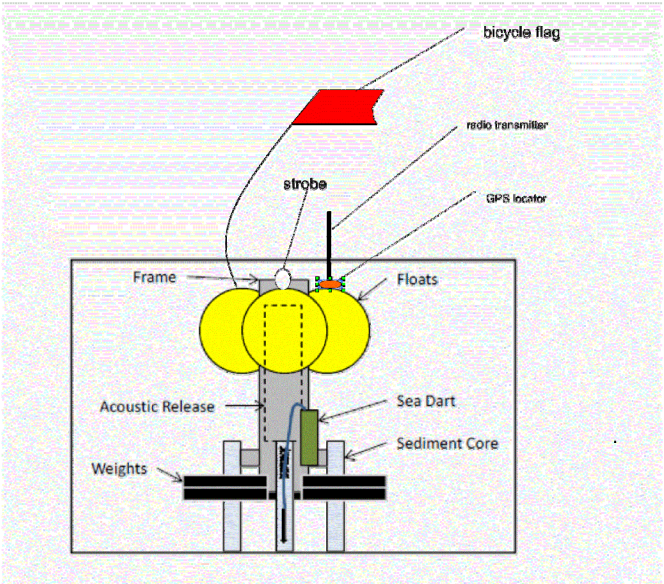

Figure 1. Cartoon of the free vehicle that buries MFC anodes in sediment, records MFC power, collects sediment samples, and returns to the surface after dumping ballast via an acoustic release.

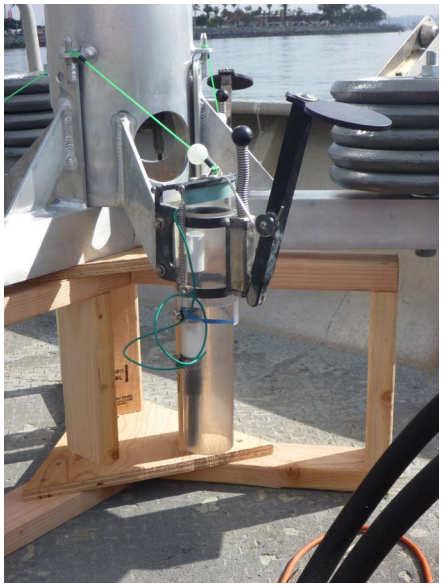

Figure 2: Sediment retaining tube with open covers and MFC anode. Ascent of cylinder away from ballast platform releases covers to close via springs.

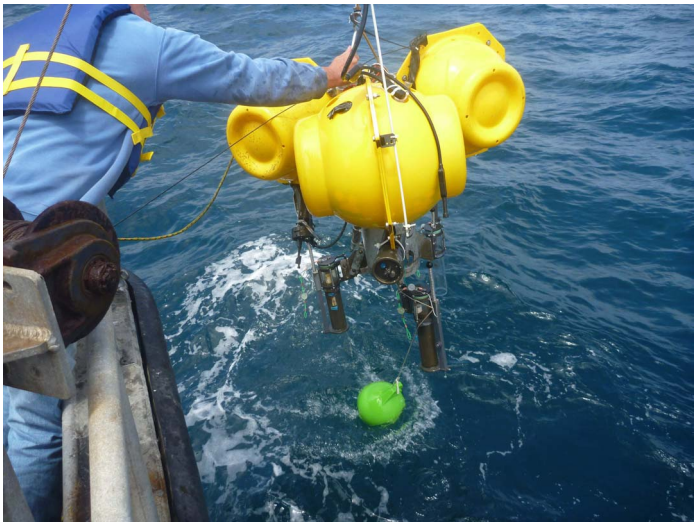

Figure 3: Recovery of MFC vehicle with full sediment tubes.

B. *Laboratory MFC in pressure vessel*

Figures 4-5 show a cartoon and photographs of the laboratory setup, respectively. The pressure vessel necessarily requires a continuous supply of oxygenated seawater to maintain the flow of electrons from the anode in the sediment to oxygen in the overlying water via the cathode. The anode, cathode and recording electronics are the same as those deployed during in situ measurements. A high pressure pump maintains a steady flow rate while an adjustable valve maintains pressures up 700 bar. The pump, valve and water bath which controls pressure vessel temperature are computer controlled. Typical flow rates are 15 ml min^{-1}, empirically determined to maintain a cathode voltage of approximately 0.35 v relative to a Ag/AgCl reference electrode, comparable to what would be measured in seawater saturated with oxygen.

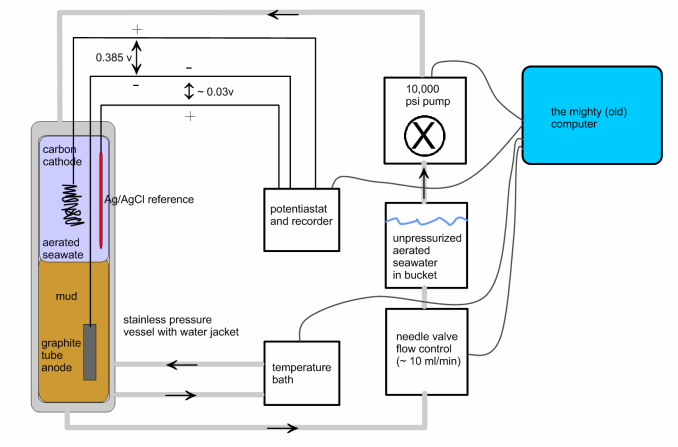

Figure 4: Laboratory MFC in pressure vessel, meant to mimic deep sea conditions of in situ measurements.

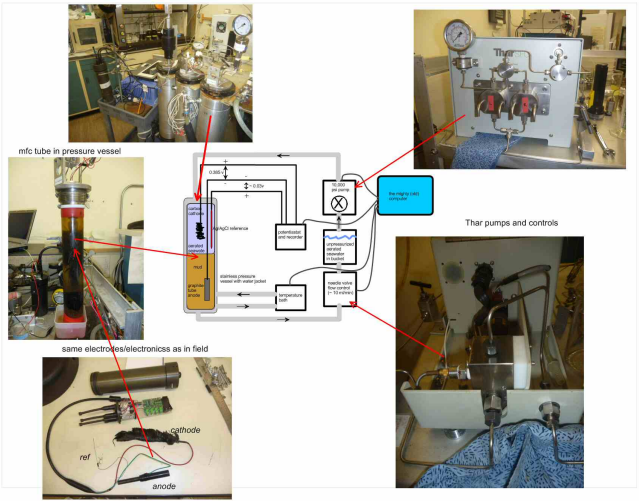

Figure 5: Photos of the high pressure laboratory system.

III. RESULTS

A. *Deep water MFCs*

Deployment of the MFCs on the free vehicle was made in progressively deeper water. Figure 6 shows the locations of the current set of data, first at 5 m in the boat channel off the Marine Corps Recruiting Depot (MCRD), then at 10 m off the bait barge in San Diego Bay, then at 100m depth and finally at 1000 m depth. Deployments typically lasted three to four weeks to allow the fuel cells to reach steady state. Figure 7 plots power output as mW m^{-2} of anode surface area. Note the log10 scale on the power axis. The power output at the 5 m location off MCRD is typical of earlier measurements at this site with the 1.3 cm (0.5 in.) diameter carbon fiber tube anode we

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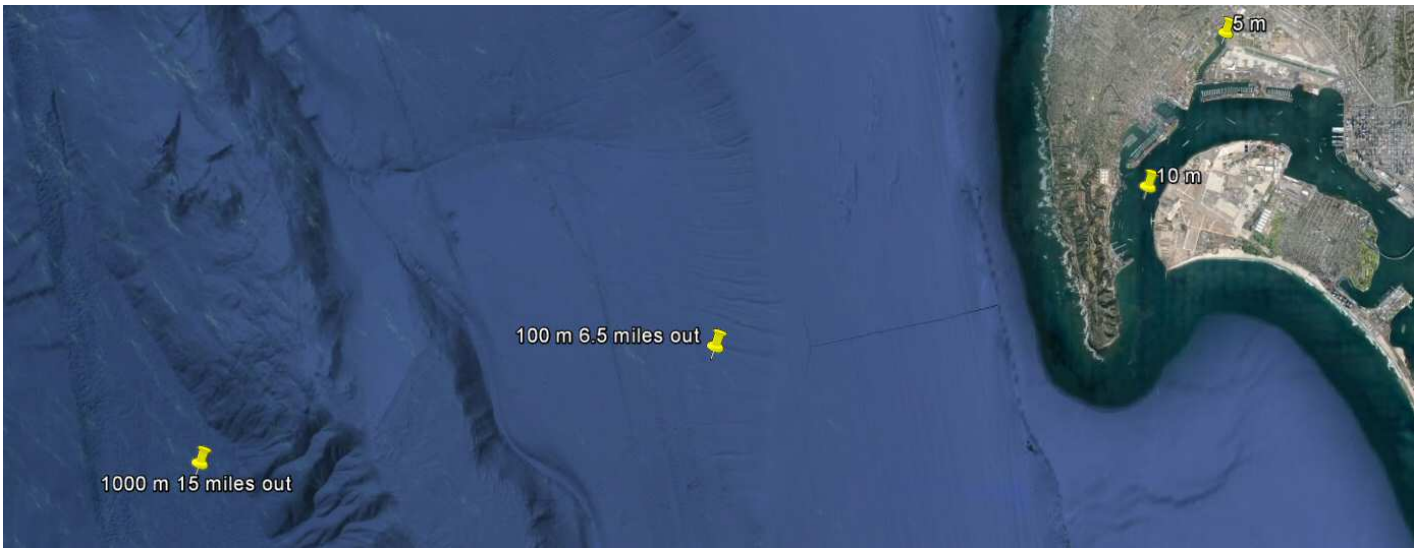

Figure 6: MFC deployment on the free vehicle off San Diego in progressively deeper water.

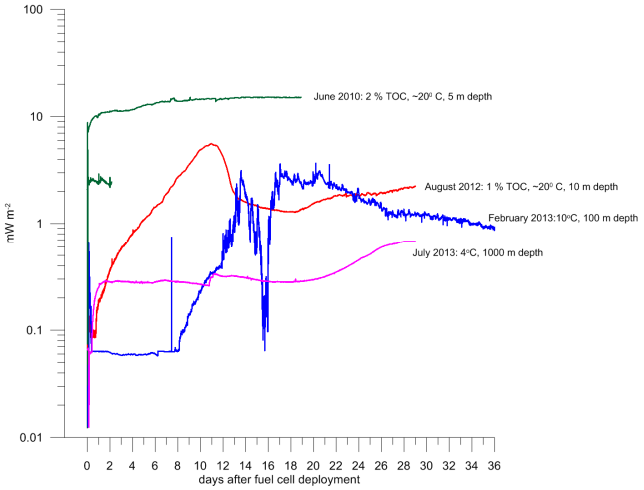

Figure 7: MFC output at various depths and temperature. Total organic carbon (TOC) data is not yet available for 100 m and 1000 m sediments.

were using in earlier measurements [4]. The same site will produce approximately 100 mW m^{-2} anode if graphite plate or carbon fiber cloth is used. We deploy a carbon tube anode on the free vehicle because of its rigidity and strength, resulting in easy deployment into the sediment. It is unclear why the power output at 100 m was so variable over time, though there were problems during deployment when the vehicle became entangled in a tethered float used to aid in retrieval. The vehicle did not fully bury the sediment tubes, no sediment was recovered during this deployment, and use of a small cabled robot was necessary to free the vehicle from the ballast frame.

While we do not yet have organic carbon results from the sediment at 100 m and 1000 m depths, we feel that the decrease in power output with depth is like caused by the decreasing ambient temperatures, based on laboratory studies presented below.

B. Results for pressurized vesel MFCs

Figure 8 plots MFC output from shallow (5 m) sediment collected off MCRD in San Diego Bay at a variety of pressures. Figure 9A plots temperature sensitivity of the same sediment measured in situ earlier [4] Figure 9B plots the subsequent power from the same mud under a range of temperatures while the pressure was held at 500 bar. The power density between the two deployments is not directly comparable because the anode material was not the same between measurements; however, the relative impact of temperature is comparable. The dramatic power drop seen in Fig 9B, in light of Figure 8, we believe is due to temperature. On restoring ambient pressure and temperature in the pressure vessel, power output has fully recovered to earlier levels. Unpublished data from our laboratory, using a different electrode scheme, have shown that the power output from 1000 m sediment collected off the Monterrey Canyon (courtesy Clare Reimers and Peter Girguis) is similarly affected by temperature when held at 100 bar. Unpublished data of the output power response to temperature from sediment collected at 5809 m from the Philippine Sea (courtesy Doug Bartlett) and held at 580 bar, surprisingly shows very little response to temperature. Current efforts consist of testing the 100 m and 1000 m sediments under various temperature and pressure regimes in the flow-through pressure vessel system.

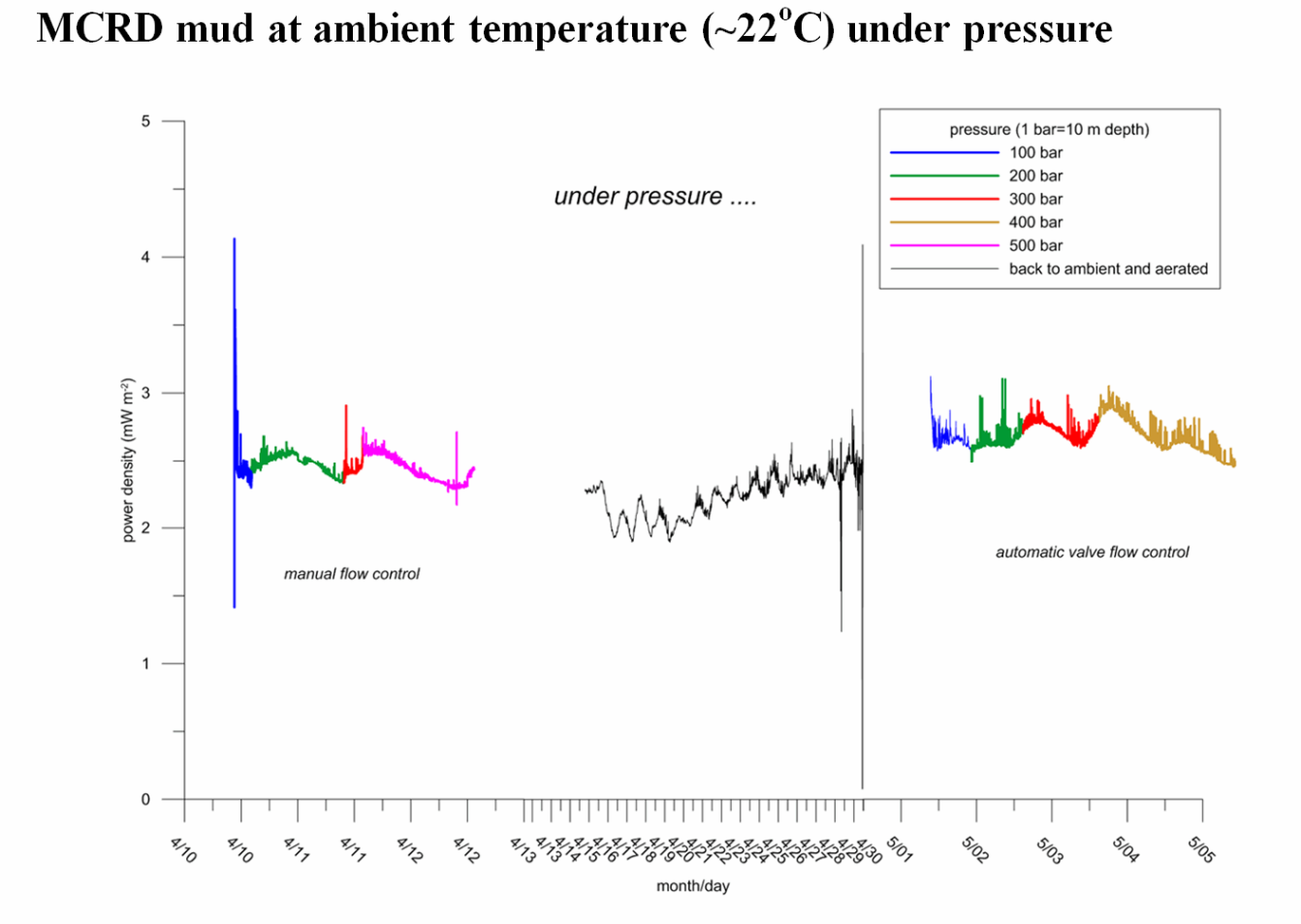

Figure 8: Effect of various pressure regimes on MFC output at ambient temperature.

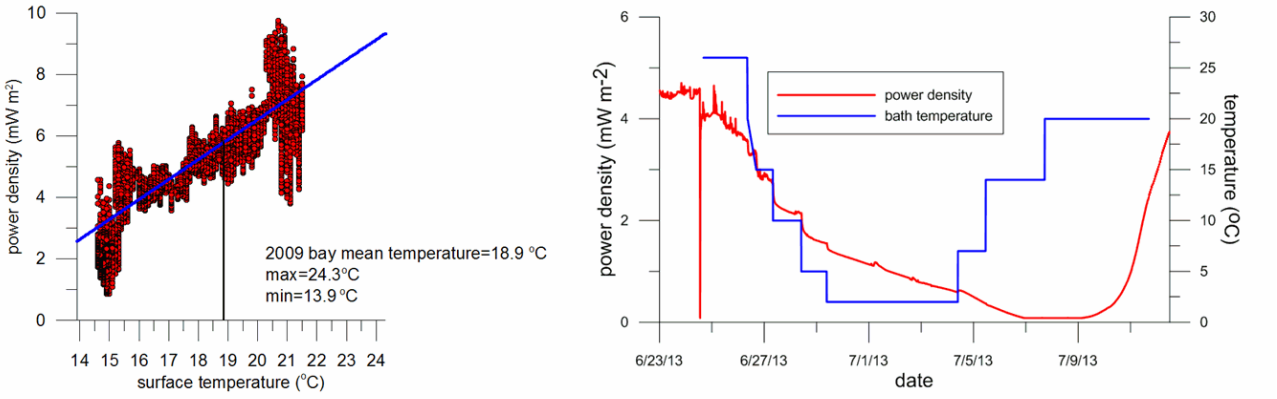

Figure 9: Temperature response of MFC in sediment from MCRD (A) in situ, (B) in the laboratory at 500 bar.

IV. Discussion and Future Directions

We have developed a deep water-deployable MFC vehicle that can take in situ measurements for a month at a time and return with sediment samples for laboratory testing and chemical analysis. We have developed a flow-through pressure vessel system that can mimic deep water conditions to approximately 6500 m and which supports a MFC identical to that deployed in the field. Both developments were completed in the early summer of 2013 so it is probably premature to derive conclusions on the MFC potential of the deep sea. However from data collected we do see a progressive decrease of MFC output with depth from 5 m to 1000 m off southern California. The laboratory studies indicate that temperature may be the primary culprit, though the amount and quality of the sediment organic fraction may be important, as well as the permeability of the sediments which control diffusion of organic material to microbes on the anode. As water depths increase away from the coast, organic material takes longer to settle to the bottom, probably allowing the more labile fraction to be stripped by microbes in the water column [e.g. 6,7]. Sediment grain size also tends to become smaller away from the coast, impeding diffusion [8].

We plan to continue in situ measurements in deeper (+4000 m) waters off Puerto Rico or Guam. We plan to make the MFC vehicle more robust by putting all the electronics within the glass floats. We hope to continue testing sediments collected from depth from cooperating research cruises. We hope to better characterize the retrieved sediment in the lab, relative to the quantity and quality of organic matter, grain size, and microbial population from reference and anode-impacted sediments collected in the sediment tubes. We will continue this work through collaboration with Naval Research Laboratory and a number of universities. This work has been generously supported by Linda Chrisey at ONR and internal programs at SPAWARSYSCEN, San Diego.

References

[1] Rabaey, K, and W, Verstraete. 2005. Microbial fuel cells: novel biotechnology for energy generation. Trends in Biotechnology 23(6) 291-298.

[2] Logan, B. E. *Microbial Fuel Cells*. 2007. John Wiley and Sons Inc. Hoboken, New Jersey.

[3] Mahadevan R., B. Ø. Palsson, and D. R. Lovley. 2011. In situ to in silico and back: elucidating the physiology and ecology of *Geobacter* spp. using genome-scale modeling. Nature Reviews Microbiology 9:39-50.

[4] Richter, K.E and A. Q. Wotowaa-Bergen. 2011. Predicting in situ sediment fuel cell potential. Oceans'11 MTS/IEEE Kona. September 19-22, 2011, Kona HI.

[5] Kato, C., L. Lina, Y. Nogi, Y. Nakamura, J. Tamaoka and K. Horikoshi. 1998. Extremely barophilic bacteria isolated from the Marianna Trench, Challenger Deep, at a depth of 11,000 meters. Appl. Environ. Microbiol. 64(4):1510-1513.

[6] Azam, F., T. Fenchel, J. G. Field. J. S. Gray, L. A. Meyer-Reil and F. Thingstad. 1983. The ecological role of water-column microbes in the sea. Mar. Ecol. Prog. Ser. 10:257-263.

[7] Fenchel. T. 2008. The microbial loop – 25 years later. J. Exp. Mar. Biol. Ecol. 366(1-2):99-103.

[8] Shepherd, R.G. 1989. Correlations of permeability and grain size. Groundwater 27(5):633-638.

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