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An Autonomous and Self-Sustained Sensing System to Monitor Water Quality near Highways

Final Report for Highway IDEA Project 125

Prepared by:

Xianming Shi and Tuan Anh Nguen, Western Transportation Institute
Hongwei Gao, Dave Catania and Gabriel Guillen, Montana State University
Colleen Courtney and Dan Schuette, WTI Research Experience for Undergraduates Program

April 2010

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An Autonomous and Self-Sustained Sensing System to Monitor Water Quality near Highways

Final Report for the IDEA Project NCHRP-125

Prepared for

The IDEA Program

Transportation Research Board

National Research Council

by

Xianming Shi (Principal Investigator) and Tuan Anh Nguyen

Corrosion & Sustainable Infrastructure Laboratory

Western Transportation Institute (WTI)

Hongwei Gao (Co-Principal Investigator), Dave Catania, and Gabriel Guillen

Electrical and Computer Engineering Department

Montana State University, Bozeman, MT 59717

and

Colleen Courtney and Dan Schuette

WTI Research Experience for Undergraduates Program

April 2010

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EXECUTIVE SUMMARY

This concept-exploration project successfully developed a prototype sensing system that is self-sustainable and can be used to autonomously, *in-situ* monitor environmental parameters in water bodies near highways. The system provides a method to rapidly, economically and safely measure environmental impact of highway construction and operation.

We used sensors, signal conditioning circuits, a microcontroller, two radio frequency (RF) transceivers, voltage regulators, microbial fuel cells, and a personal computer (PC) to develop the sensing system. The sensors are placed in the water and sense different water quality parameters; the signal conditioning circuits properly condition the signals from the sensors and provide the conditioned signals to the microcontroller; the microcontroller reads the signals from the signal conditioning circuits, processes the signals into data packets, and sends the data packets to a RF transceiver that is connected to the microcontroller; the RF transceiver sends the data packets to the RF transceiver that is connected to the PC; the PC, which can be placed in a laboratory or a office, can read the data packets from the RF transceiver and processes the water quality information contained in the data packets. The microbial fuel cells generate electricity for the sensing system using electrochemical reactions and naturally-occurring safe bacteria, whereas the voltage regulators stabilize and condition the output of the microbial fuel cells and provide properly regulated voltage to the sensors, the signal conditioning circuits, the microcontroller, and the RF transceiver connected to the microcontroller. The system was fully developed and tested and functioned mostly as expected (with a few lessons learned).

The innovation in the project lies in the coupling of *online* monitoring of water quality along highways with renewable and self-sustained energy generation, as well as the highly scalable microbial fuel cells specifically designed for water quality monitoring. While the technical concept has been successfully demonstrated, significant engineering improvements are needed to bring this technology to a market-ready state. The research team is in the process of filing a provisional patent to protect the intellectual property generated from this project, and funding will be pursued to support additional phases of this work, in order to further implement necessary improvements identified from this work (especially pertaining system capability, performance, reliability and cost-competitiveness) and to bring this technology to the marketplace and into practice.

IDEA PRODUCT

This concept-exploration project successfully developed a prototype sensing system that is self-sustainable and can be used to autonomously *in-situ* monitor environmental parameters in water bodies near highways. Implementing a system of this nature would alleviate the need for manual water sampling along roadsides. The research team is in the process of filing a provisional patent to protect the intellectual property, and funding will be pursued to support additional phases of this work, in order to further implement necessary improvements identified from this work (especially pertaining system capability, performance, reliability and cost-competitiveness) and to bring this technology to the marketplace and into practice.

The problem addressed is a NCHRP IDEA research issue, namely lack of advanced monitoring methods to rapidly, economically and safely measure the environmental impact of highway construction and operation. Our approach to this problem is to develop a sensing system that can autonomously, *in-situ* monitor the quality of water adjacent to highways at distributed point locations. We used sensors to detect different water parameters, electronic circuits to condition the signals from the sensors, a microcontroller to read the signals from the electronic cirucits and convert the signals into data packets, and a RF transceiver to tranmit the data packets to a remote PC. Moreover, we used microbial fuel cells, devices that can generate electricity through electrochemical reactions and maintain the reactions using a type of safe bacteria, along with voltage regulators, to power the sensors, electronic circuits, the microcontroller, and the RF transceiver. Since the bacteria used in the microbial fuel cells are ubiquitous in aqueous environments, the microbial fuel cells have renewable and sustainable energy-generating capability and therefore do not need to be replaced before the anode material is significantly degraded (a theoretical service life of twenty years or more).

CONCEPT AND INNOVATION

As shown in Figure 1, the developed system consists of microbial fuel cells, voltage regulators, sensors, signal conditioning circuits, a microcontroller, two RF transceivers, and a PC. The sensors convert different water quality parameters into electric signals; the circuit conditioning circuits properly condition the signals from the sensors and provide the conditioned signals to the microcontroller; the microcontroller reads the signals from the signal conditioning circuits, processes the signals into data packets, and sends the data packets to the RF transceiver that is connected to the microcontroller; the RF transceiver connected to the microcontroller sends the data packets to the RF transceiver attached to the PC; the PC can read the data packets and process the water quality information contained in the data packets.

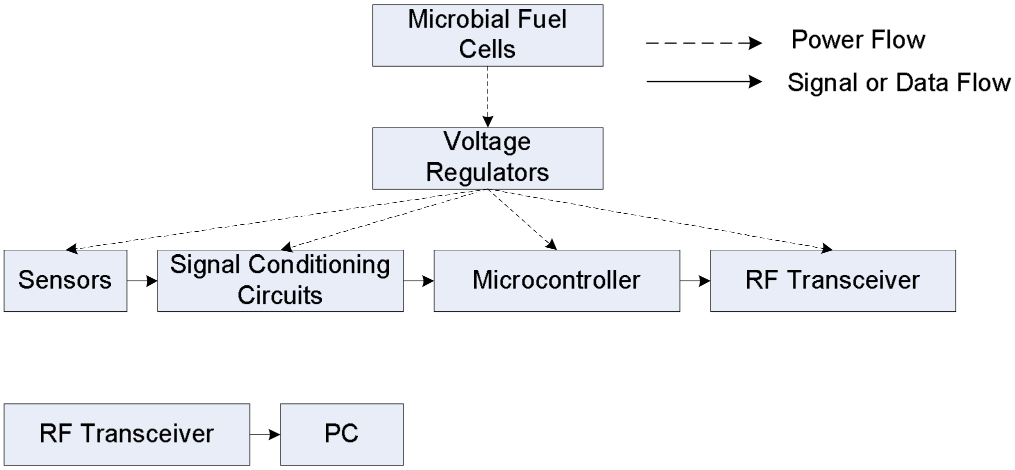


Figure 1. Block diagram of the developed sensing system.

The system aims to measure physical and chemical properties of water at discrete time intervals and at distributed point locations. The concept is innovative in two aspects as follows. First of all, coupling the in-situ monitoring of water quality along highways with renewable and self-sustained energy generation is a novel idea. For monitoring water quality adjacent to highways, current practice is to periodically collect samples and manually bring the samples back to laboratories for analyses. While there have been reports of near-real-time monitoring of water quality in lakes and other aqueous environments, the practices are not feasible for wide-area monitoring of water quality along highways as they used conventional batteries and/or solar panels as the power supply. Microbial fuel cells (MFCs) offer specific advantages over other renewable energy conversion methods, such as photovoltaic panels, principally in terms of compact configuration and 24-hour operation. Microorganisms, such as bacteria readily available in the natural environment, are fascinating alternatives to transition metal catalysts used in chemical fuel cells since they are environment-friendly, renewable, and inexpensive. MFCs that harvest energy from the environment could potentially be made self-sufficient with just the pre-treated electrodes and an input of nutrients from the environment. As such, they would be ideal for a host of autonomous applications that demand minimum amount of maintenance or can operate in a reliable manner without any servicing. Secondly, the innovation lies in the highly scalable MFC specifically designed for water quality monitoring. By coupling a sacrificial anode with a bio-cathode, the MFC design we proposed is different from and likely much better than existing ones. Traditional MFCs feature a bio-anode and suffer low levels of energy-generating capability that hinder their practical application. Using biomineralized manganese oxides (other than oxygen) as its cathodic reactants and a sacrificial anode (other than a bio-anode) for its anodic reaction, this novel MFC promises not only higher output of electricity but outstanding scalability to further boost the output in order to meet the requirements of a water quality monitoring system. The new design makes it possible to connect multiple MFCs in series or in parallel in a compact array, the energy from which would be sufficient to power water quality sensors, telecommunication devices and other components in the system. Design of the power management system will demand innovation as the output of MFCs is prone to fluctuations in environmental conditions and needs to be regulated intelligently.

In this project, we focused our innovation in the design of microbial fuel cells (MFCs) and the associated power management system, and used commercially available products for sensors and telecommunication devices. Depending on the parameters of concern, various off-the-shelf water quality sensors can be easily incorporated into the system, with minor modifications to the system.

The system will be self-sustained and thus allow long-term and wide-area monitoring with minimum amount of maintenance, as it will harness the native population of manganese-oxidizing bacteria abundant in natural waters to generate electricity and harvest renewable energy from the environment.

Sensors

While there are many environmental parameters and agencies of great interest to the State Departments of Transportation (e.g., BOD, COD, herbicide concentrations), it is impossible to monitor all these parameters or agencies in this proof-of-concept project due to the limited project time period and project budget, and availability of commercial sensors. Therefore, in this project, we chose to use sensors to monitor some basic and useful water quality parameters - pH, chloride ion concentration, and temperature. Nonetheless, it is possible to incorporate more commercially available sensors of other parameters into the current sensing system with minor changes of the electric circuits in the system, depending on the specific user needs. The additional power requirements can be addressed by increasing the number or dimensions of MFCs coupled together to provide the energy for the sensor network.

pH and Chloride Sensors

pH and chloride sensors generate voltage signals proportional to the pH and the logarithm of the chloride ion concentration respectively. These signals must be amplified before they can be properly interpreted by the microcontroller.

Temperature Sensor

The temperature sensor is a standard thermistor which represents changes in temperature with changes in resistance. We used a voltage-divider as shown in Figure 2 to convert the changes in the resistance to changes in voltage and used signal conditioning circuitry to condition the voltage.

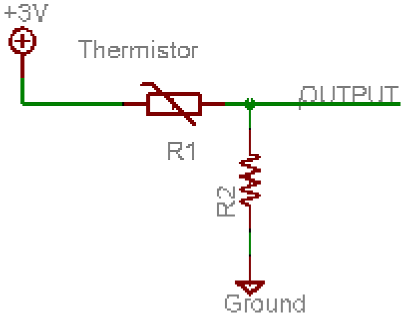


Figure 2. Voltage-divide to convert changes in resistance of temperature sensor to changes in voltage.

Signal Conditioning Circuits

The output voltage of the sensors must be amplified to the appropriate levels before they can be read by the analog-to-digital converter in the microcontroller. We used low power operational amplifiers in a non-inverting setup to amplify the output voltage of the sensors. The signal conditioning circuit is shown in Figure 3.

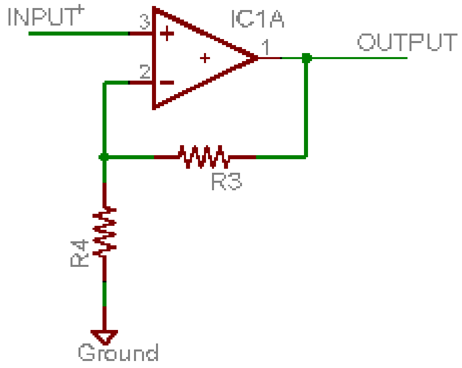


Figure 3. Signal conditioning circuit using non-inverting operational amplifier.

Microcontroller

The microcontroller uses its built-in analog-to-digital converter to convert the voltage signals from the signal conditioning circuits to numerical data, format the data into data packet, and then send the data packet to the RF transceiver for transmission. The flow chart for the microcontroller is shown in Figure 4. The cycle repeats at an interval determined by the user and power restrictions.

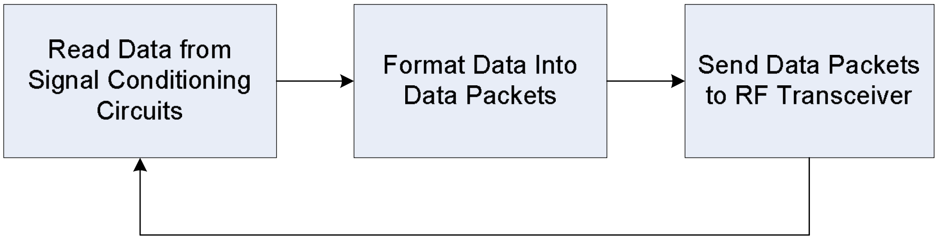


Figure 4. Flow-chart for the microcontroller.

RF Transceiver

We used 900MHz RF transceivers to transmit data from the microcontroller to the PC over a long distance (about 1-5 miles up to the power budget).

Microbial Fuel Cells

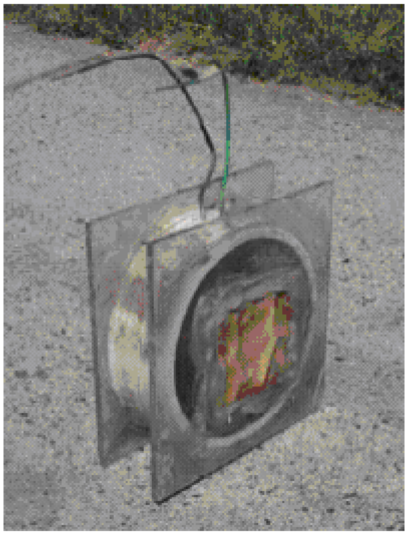


Figure 5. First-generation prototype of the self-sustainable power supply.

Different from traditional MFCs which utilize a bio-anode and tend to have limited scalability and low energy generation, our design of the power supply features a bio-cathode (with manganese oxides as renewable cathodic reactants) coupled with a sacrificial anode. So when there are little microbial activities, it is in essence a battery; when there are significant microbial activities, it becomes a MFC. Based on this concept, we developed the first-generation prototype of the self-sustainable power supply with a few MFCs coupled in series (as shown in Figure 5).

More fundamental knowledge relevant to this innovative power supply can be found at: Nguyen, T.A., Lu, Y., Yang, X., and Shi, X. Carbon and Steel Surfaces Modified by *Leptothrix discophora* SP-6: Characterization and Implications. *Environmental Science & Technology* 2007, *41*(23), 7987-7996. http://dx.doi.org/10.1021/es071178p. Note that the detailed design of the MFCs or the power electronics is not disclosed in this report, as we are in the process of filing a provisional patent to protect the intellectual property.

This concept offers a feasible solution to the long-term, wide-area, *in-situ*, and near-real-time monitoring of water quality parameters, as it will harness the native population of manganese-oxidizing bacteria (e.g., *L. discophora*) abundant in natural waters to generate electricity and harvest renewable energy from the environment. As an essential micronutrient for most organisms, manganese (Mn) is Earth's second most abundant transition metal next to iron.

In natural waters, soluble Mn(II) can reach up to millimolar concentrations, even in the presence of oxygen (Tebo et al., 2004), and biological catalysis has been well established as the dominant mechanism of oxidizing Mn(II) to insoluble Mn(III, IV) oxides in circumneutral freshwater (Ghiorse, 1984; Nealson et al., 1988).

Mn(II)-oxidizing microorganisms, primarily bacteria and fungi, are ubiquitous in nature and accelerate the rate of Mn biomineralization several orders of magnitude faster than either abiotic catalysis on mineral surfaces or homogeneous oxygenation in aqueous solution (Tebo et al., 2005). This was demonstrated by *in-situ* immersion of 316L stainless steel into a freshwater creek, where open circuit potential of the steel was increased by almost 0.4V in a week resulting from Mn biomineralization (Dickinson et al., 1995).

Manganese-oxidizing bacteria are likely to survive cold temperatures or other relatively harsh conditions in the field environment. For instance, the 'Wild-type' *L. discophora* are mostly the sheath-forming strain SP-6, which can be maintained indefinitely in slow growing conditions at temperatures between 20°C and 25°C. For culture management, it can be stored at 4°C and -80°C (Emerson et al., 1992). The bacteria thrive under certain conditions: temperatures between 10°C and 40°C and a pH between 6 and 8.5 are ideal for the biofilm growth of such bacteria (Zhang et al., 2001).

It is noteworthy that the significant ennoblement of potential can be achieved with a small amount of manganese oxides, as demonstrated by a study where 6% coverage of the metal surface increased the open circuit potential of 316L stainless steel from -200mV to +350mV$_{SCE}$ (Dickinson et al., 1996). Dr. Shi studied the Mn biomineralization phenomena by *L. discophora* SP-6 (Shi et al., 2002a) and argued that the following electrochemical half-reactions are responsible for the ennoblement of the potential:

$$MnO_2 + H^+ + e^- \rightarrow MnOOH \qquad E^0 = +0.81\ V_{SCE} \qquad (1)$$

$$MnOOH + 3H^+ + e^- \rightarrow Mn^{2+} + 2H_2O \qquad E^0 = +1.26\ V_{SCE} \qquad (2)$$

With the overall reaction shown in Equation (3), the half-cell equilibrium potential of a noble cathode (such as graphite) covered with biomineralized Mn oxides could reach +360mV$_{SCE}$, or +0.60V$_{SHE}$,

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad E^0 = +1.28\ V_{SCE}, \text{ i.e., } E'_{pH=7.2} = +0.36\ V_{SHE} \quad (3)$$

Biomineralized manganese oxides can be used as cathodic reactants significantly superior to oxygen. First, they are some of the strongest oxidizing agents (next to oxygen) found in the natural environment. In many natural waters, microbial activities lead to the formation of particulate Mn oxides with average oxidation states exceeding 3.4 (Tebo et al., 2004). Second, the reduction of manganese oxides deposited by *L. discophora* increased the cell potential by approximately 300 mV and delivered a current density up to 2 orders of magnitude higher, compared with those reached with the reduction of oxygen (Rhoads et al., 2005). More importantly, manganese oxides are in direct contact with the electrode, where the cathodic reaction is thus not limited by the mass transfer process of cathodic reactants. Finally, manganese oxides are renewable. When used as a cathode for the MFC, manganese oxides are reduced to Mn(II), which in return is microbially re-oxidized. This sequence of events produces renewable cathodic reactants, manganese oxyhydroxide and manganese dioxide, in direct contact with the electrode (Shi et al., 2002a).

Voltage Regulators

The voltage level of the microbial fuel cell is not appropriate for powering the electric circuits or components in the system and the voltage fluctuates. Therefore it is necessary to convert the voltage of the fuel cell to appropriate levels and regulate the voltage. In the project, we used voltage regulators to accomplish this goal.

INVESTIGATION

We completed the project in three stages.

Work in Stage one included selecting water quality sensors, communication devices, and a microcontroller for the sensing system—and analyzing the voltage, current, and power requirements for all of the selected components. Design guidelines for the fuel cells were developed and a DC-DC converter was designed specifically for the system. Finally, a microbial fuel cell (MFC) was designed by a team at the Western Transportation Institute (WTI). Anode and cathode materials were selected and tested to maximize MFC performance. Preliminary results indicated that the developed MFC should be able to provide the necessary power to the sensing system.

Work on Stage two included fabrication and testing of the MFCs. The performance of a single MFC under various conditions was tested. Subsequently, an array of MFCs was built for preliminary testing. Based on test results, improvements to the design of both the single MFC and the array of MFCs were made. The scalability of the current MFC design was tested to maximize the sustainable power output of MFCs and minimize their internal resistance. The sustainability of the MFC array as a power supply was also tested. The performance of the MFC array was evaluated under various simulated field conditions (varying temperature, pH, and cell density of *L. discophora*). Water quality sensors were purchased and tested. A low power microcontroller, a 900 MHz RF transceiver, and signal conditioning circuitry were built or purchased then tested. Firmware for the microcontroller was developed so that it could read data from the signal conditioning circuitry and transmit to a remote PC. All sub-systems were constructed, tested, and assembled into an integrated system. The system's power supplies were also tested and fine-tuned.

In Stage three, the entire system was tested over the span of several weeks in a local stream during varied weather conditions. The MFC array was unable to provide enough power to sustain the function of the circuitry over a test period that included both temperature and sunlight fluctuations. The microcontroller successfully executed the proper system functions based upon the measured output power of the MFC array. In battery-powered field demonstration, the RF transmitter was tested to a maximum range of 250 meters with suboptimal antenna alignment due to the local terrain. Data was transmitted on a 60 second interval and proved to be within acceptable tolerances for the chosen sensors (except pH sensor after 24 hours). While the technical concept has been successfully demonstrated, significant engineering improvements are needed to bring this technology to a market-ready state.

Stage One: Design or Selection of Component

In Stage one, we completed the following six tasks.

Task 1 Selection of sensors

Task 2 Selection of RF transceivers

Task 3 Selection of Microcontroller

Task 4 Design of Data Collecting, Transmitting, and Receiving System

Task 5 Design of microbial fuel cells.

Task 6 Design of voltage regulators

We considered performance, functionalities, and cost when we selected the sensors, the microcontroller, and the RF transceivers. The manufacturer and the model number of the selected parts are listed in Table 1.

Table 1. Manufacturer and model number of selected sensors, RF transceivers, and microcontroller.

	Sensors	*RF transceiver*	*Microcontroller*
Manufacturer	Instrumentation Northwest Inc	Digi International	Microchip
Model #	TempHion-3	9XCite model XC09-009NSC	PIC18F2620

All the selected sensors-a temperature sensor, a pH sensor, and a chloride ion sensor-are included in one single package (priced at $795), the specifications of which are provided in Table 2.

Table 2. Specifications of TempHion-3 4T851 sensor packet

TempHion T-3 Packet Specifications			
Power Supply	8 to 24 Volts	*Stability*	< 10% in 12 months
Operating Range	0 to 60˚ C	*Accuracy*	+/- 5%

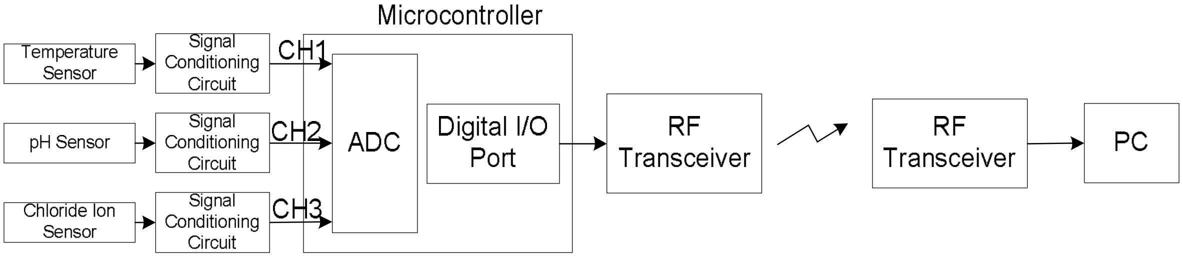


Figure 6. Block Diagram of Data Collecting, Transmitting, and Receiving System.

After selecting the sensors, the microcontroller, and the RF transceivers, we also designed the data collecting, transmitting, and receiving system. The block diagram of the system is shown in Figure 6. In the data collecting, transmitting, and collecting system, the sensors sense environmental parameters in the water bodies; the signal conditioning circuits adapt output of the sensors to requirement of the built-in Analog-to-Digital Converter (ADC) of the microcontroller; the microcontroller uses its ADC to read the data from the signal conditioning circuits and uses its digital I/O port to send the data to the RF transceiver connected to the microcontroller; the RF transceiver collected to the PC receives the data and sends the data to the PC.

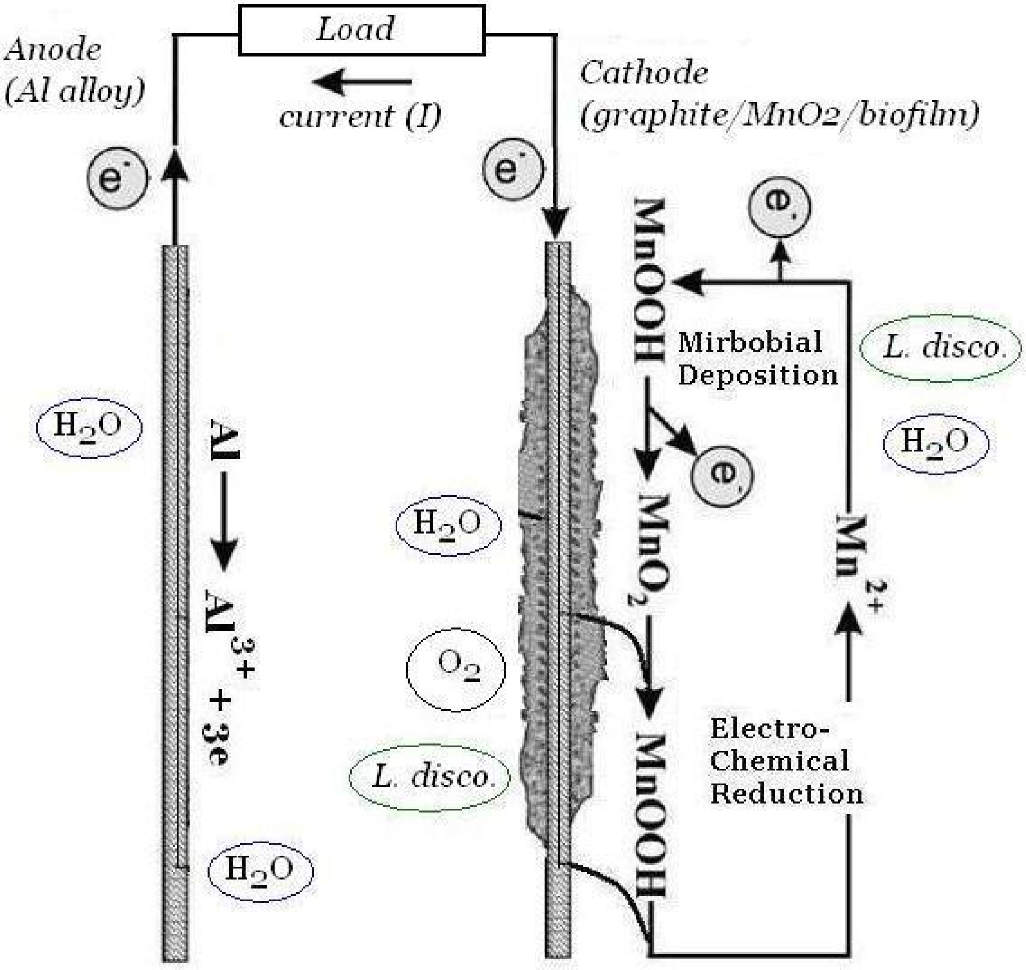


Figure 7. Schematic of the proposed MFC, consisting of a sacrificial anode of aluminum alloy and a cathode of graphite covered by manganese dioxide and biofilms of manganese-oxidizing bacteria, *L. discophora* SP-6.

We designed the microbial fuel cells in Stage one. The initial design of the MFCs is shown in Figure 7. Each MFC will consist of a sacrificial anode and a graphite cathode coated with manganese dioxide and biofilms of*L. disco*. SP-6. Note that there is a cycling of manganese at the surface of cathode, including biomineralization of divalent manganese and electrochemical reduction of manganese oxides. Native population of manganese-oxidizing bacteria (e.g.,*L. discophora*) has demonstrated the capability to accumulate the managese ions in streams and deposit manganese oxides, and this continuous process will replenish the minerals on the surface of graphite electrode providing the positive potential. In addition, there is no need to add any redox mediator to the cathodic compartment because the biomineralized manganese oxides were deposited on the surface of the electrode and were reduced directly by electrons from the electrode.

In the project we selected Al-Zn-Si-In (Aluminum alloy 24779, 4-6.5 wt% Zinc, 0.08-0.12 wt% Silicon, 0.014-0.02 wt% Indium) series of modern aluminum anodes, in light of their 1) high current capacity under variable conditions and over time, 2) desirable anode potential and its reliability over time, 3) environmentally-friendly characteristics, and 4) being the most economical choice among different types of anode in aqueous cathodic protection systems. Aluminum anodes are known to remain clean and active in fresh water, despite the presence of bacteria and fungi. Such anodes should last for years, if not decades, according to field evidence from the cathodic protection systems that routinely use them for corrosion protection. A similar Al alloy anode has a current capacity in the region of 2500 Ah/kg. Laboratory testing shows that the open circuit potential (OCP) of graphite electrode versus this aluminum alloy (with exposed surface area of 6 cm^2) in water taken from a Bozeman stream ranged between 0.95 and 1.1 V. Given the external load of a 110-Ω resistor, this power supply gave a current of 0.09 mA, due to the loss of energy to the internal resistance of this power supply. When we electroplated the graphite electrode with manganese dioxide (MnO_2), the output voltage and current was improved to 1.2-1.4V and 0.18 mA respectively. This could be further improved by reducing the distance between the anode and the graphite electrode, as well as by increasing the dimensions of the electrodes. We also tested the performance of this MFC in the presence of added bacteria (*L. discophora* SP-6), which significantly increased the output current of the MFC to approximately 0.46 mA. This is expected to be further improved by applying a micro-filter membrane onto the Al alloy surface.

We also designed voltage regulators in Stage one. The voltage regulators were intended to step down the 12V voltage of the microbial fuel cells to 9V for sensors and 3V for other electronics in the sensing system. The regulators are switched-mode step-down DC/DC converters, whose topology and operation are shown in Fig. 8.

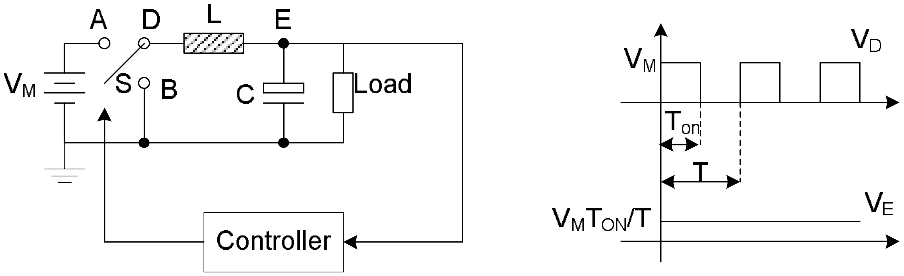


Figure 8. Topology and operation of step-down DC/DC converter.

A switch-mode step-down DC/DC converter consists of a single pole-double throw switch S, an inductor L, a capacitor C, and a controller. The controller controls the position of S so that S moves to node A and node B alternately with a constant frequency such as 100 KHz. When S moves to node A, voltage of node D, V_D, equals voltage of the MFCs V_M, while V_D equals zero when S moves to node B. Therefore, S chops MFCs' voltage into a square wave voltage V_D, whose waveform is shown in Figure 8. The inductor and capacitor form a low pass filter, which removes high frequency components of V_D but keeps the DC component, which, according to Fourier analysis, is given as:

$$V_E = \frac{1}{T}\int_0^T V_D dt = \frac{1}{T}[\int_0^{T_{ON}} V_D dt + \int_{T_{ON}}^{T} V_D dt] = \frac{1}{T}[\int_0^{T_{ON}} V_M dt + \int_{T_{ON}}^{T} 0 dt] = V_M \frac{T_{ON}}{T} \quad (4)$$

Where V_E is the output voltage of the low pass filter or the output voltage of the converter; T is the switching period of the switch and is kept constant by the controller; Ton is the duration when S stays at node A in one switching period and is adjusted by the controller. Equation (4) shows that Ton controls V_E. The controller reduces Ton when V_E is above the reference value and increases Ton when V_E is below the reference value, to regulate V_E.

As the project progressed, we found the voltage of the microbial fuel cells were actually much lower than 12V-between 4V and 5.5V. As a result, we designed a step-up DC/DC converter in the later stage to supply 9V voltage to the sensors (we still used a DC/DC converter to step-down the microbial fuel cell voltage to 3.3V for the microcontroller and other electronics in the system). The topology of a step-up DC/DC converter is shown in Figure 9.

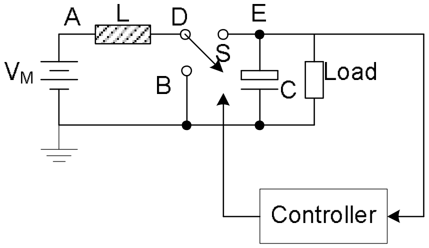


Figure 9. Topology of step-up DC/DC converter.

A switch-mode step-up DC/DC converter also consists of a single pole-double throw switch S, an inductor L, a capacitor C, and a controller. The controller controls the position of S so that S moves to node E and node B alternately with a constant frequency such as 100 KHz. When S moves to node B, the inductor is connected to and charged by the microbial fuel cells; when S moves to node E, the inductor is connected to capacitor C and delivers energy to capacitor C and the load. The output voltage of the converter, V_E, is given as:

$$V_E = V_M \frac{T}{T_{ON}} \tag{5}$$

Where V_E is the output voltage of the converter; T is the switching period of the switch and is kept constant by the controller; Ton is the duration when S stays at node Bin one switching period and is adjusted by the controller. Equation (5) shows that Ton controls V_E. The controller reduces Ton when V_E is above the reference value and increases Ton when V_E is below the reference value, to regulate V_E.

Stage Two: Fabrication or Testing of Each Component

In Stage two, we completed the following tasks.

Task 7 Construction and testing of microbial fuel cells

Task 8 Construction and testing of voltage regulators

Task 9 Construction and testing of data collecting, transmitting, and receiving system

In this Stage, we built and tested the microbial fuel cells. For a conventional 12-V car battery, it consists of 6 cells (in series) of 2.1 volts each, and each cell is situated in a separated compartment containing electrolyte. However in our MFCs for water quality monitoring, each and every MFC is immersed in the same stream water and it is difficult to separate them in closed compartments as in the case of car battery. To address this challenge, the WTI team proposed a design to connect single MFCs in series while using small cation-exchange membrane and anion-exchange membranes to separate the individual MFCs and using large polyester porous membranes within each MFC.

In order to improve the sustainability of the MFC array as power supply under external load, we prepared custom-made cathode using a slurry method to mix MnO_2 with carbon powder, instead of the electroplating of a thin MnO_2 layer on graphite. This is a *key innovation* and dozens of formulations were tested before a best-performing mix was identified and selected for use in this application.

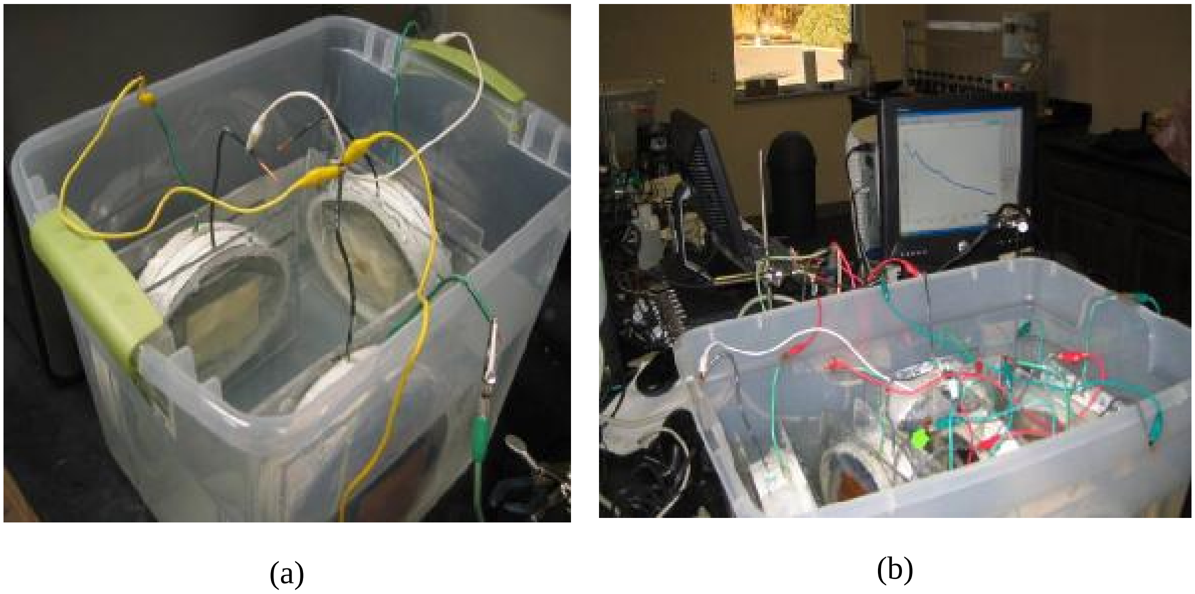

(a) (b)

Figure 10. MFC arrays with (a) three and (b) five single cells coupled in series respectively.

Some sensors we selected for water quality monitoring demands a high electric potential from the power supply to enable their operation. Conceptually, by coupling several MFCs in parallel it can increase only the output current of the power supply as a result of increased surface area, but still limited its output potential. On the contrary, by coupling several MFCs in series it can increase the output potential of the power supply. However, increasing the number of MFCs in such an array may not necessarily benefit the output current of the power supply, considering the increased internal resistance of the MFC array. Figure 10 presents the digital photos of several MFC arrays with three and five single cells coupled in series respectively. Laboratory testing of MFC arrays with 3, 5 and 7 cells in series showed an output voltage and current in the range of 4-7 V (without load) and 5-14 mA (over a 100-Ω resistor) respectively, from which their internal resistance was estimated to be approximately 300Ω, 400 Ω, and 1200 Ω, respectively. The array with five cells was selected as the power supply for our water sensing system for its collectively better performance in both the output potential and the output current.

For the selected power supply, i.e., the one with 5 single MFCs coupled in series and each MFC featuring a custom-made cathode, we further tested its performance as a function of some known influential factors. Specifically, we tested the output potential and output current of the power supply over time, in the presence of *L. discophora*. We controlled the water temperature, pH and *L. discophora*. content in the test medium (stream water taken from a Bozeman source) and monitored the MFC array's performance as a function of various conditions reasonably simulating the filed conditions such a power supply may encounter when used for water quality monitoring along highways.

First, we tested the effect of *L. discophora* cell density, using stream water at room temperature (73^{o}F, pH 8.5) at two levels of bacterial cell density: 5×10^6 and 5×10^7 cells/ml. It is interesting to note that while the higher bacterial cell density only slightly enhanced the output potential (from 6 to 6.5 V), it more than doubled the output current of the power supply (from 5.8 mA to 13.8 mA, under a 100-Ω load), indicating a dramatic drop in its internal resistance possibly as a benefit of biomineralization.

Second, we tested the effect of the stream water's pH, using stream water at room temperature (73^{o}F, cell density of 5×10^7 cells/ml) at two levels of water pH: 7.0 and 8.5. Compared with the neutral water (5.8 V, 8 mA), the pH 8.5 water led to both higher output potential (~6.5 V) and higher output current (~12 mA). One possibility is that the more alkaline aqueous solution facilitated the biomineralization (Equation 6) and enhanced the stability of MnO_2 at the cathode.

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e \quad (6)$$

Finally, we tested the effect of the stream water's temperature, using stream water (pH 7, cell density of 5×10^7 cells/ml) at two water temperatures: 40^{o}F and 70^{o}F. While the higher water temperature only slightly improved the output potential (from 5.4 to 5.6 V), it significantly enhanced the output current of the power supply (from 5.5 to 8 mA), indicating a dramatic drop in its internal resistance possibly as a benefit of biomineralization.

Overall, it can be concluded that such a power supply can still work when the water temperature, pH, or bacterial cell density drops to a reasonable degree, but its output energy will be less and it will take longer time to accumulate sufficient energy to power a set of water quality sensor readings and the wireless transmission of the data.

In Stage two, we also built and tested the voltage regulators and the data collecting, transmitting, and receiving system. The built voltage regulators and the data collecting and transmitting system are shown in Figure 11.

Figure 11. Voltage regulators and data collecting and transmitting system.

On the left-hand side of Figure 11 are the voltage regulators placed on a printed circuit board; in the middle are the circuit conditioning circuits and the microcontroller placed on a printed circuit board; on the right-hand side is the RF transceiver connected to the microcontroller placed on a another printed circuit board.

The data collecting system is shown in Figure 12. It consists of a RF transceiver and some supporting circuits, all placed on a printed circuit board. The board should be connected to a PC through a USB port.

Figure 12. Data receiving system.

Stage Three: Assembly and Testing of the System

In Stage three, we completed the following two tasks.

Task 10 System integration and testing in the laboratory

Task 11 Field evaluation and refinement

We assembled the entire sensing system and tested the system in the laboratory and in the field. The test procedures and results are as follows.

Sensors

The sensors were calibrated and tested using a laboratory standard solution for pH and chloride ion concentration. The pH sensor was tested with three common solutions with known pH values of 4, 7, and 10. This range ensures that the sensor produces reasonable output across the extremes of the specified operating range. A series of tests was conducted consisting of a rapid cycle test and an aging test. The cycle test identified the sensor transient response time by alternately testing the three pH solutions and monitoring the length of time required for the output to stabilize. The sensor was found to have a response time on the order of 30 seconds at room temperature. The response time varies as the solution temperature changes, warmer solutions produced faster response times whereas cooler solutions slowed the response time. This temperature dependence is due to the temperature dependence of the ion activity and is not unique to this particular sensor. The aging test identified long-term stability of the sensor output. This test was conducted over a 12-day period resulting in a very low drift. The readings were mostly affected by temperature variations due to the ambient temperature. No noticeable output variations could be attributed to the sensor other than the temperature due to the magnitude of this effect on the output.

Similarly, the chloride ion sensor (ISE) was tested with a range of known salt solutions ranging from 0.1 mg/L to 10000 mg/L in decade steps. The test range far exceeded what is expected in most test environments and helped identify the output characteristics of the sensor. The results indicated that the ISE sensor was capable of detecting chloride levels as low as 0.1mg/L but the output was unstable and tended to fluctuate due to errors inherent in the sensor electronics. Across the entire range the sensor was highly nonlinear, necessitating a small calibration range that represents the expected typical values observed in the field environment. As such, a range of 100 mg/L to 1000 mg/L was chosen, leading to relatively accurate readings. The current calibration curves allows for a reading within 12% of the actual value at the high end of the concentration and within 1% of the actual value at the lower end of the concentration, using a simple logarithmic curve fitting equation. The ISE channel is very sensitive to temperature changes and will therefore require a compensation scheme. The sensor module provides a thermistor output with a well-characterized output, which was not implemented in the testing scheme but can be easily used to adjust the ion readings in future work.

Microcontroller and other electronics

The microcontroller and other electronics were tested for extended periods of time to ensure reliability of the digital hardware and firmware design. After twelve days of continuous operation including power cycling and controlled power brown-outs, the microcontroller and the electronics performed as designed. No errors in firmware were detected. All functions executed as and when required. The microcontroller master reset circuitry assured that the unit resets properly even when the voltage sags slowly.

Electronics

The electronics were tested for extended periods of time to ensure reliability of the digital hardware and firmware design. After twelve days of continuous operation including power cycling and controlled power brown-outs, the digital electronics performed as designed. No errors in firmware were detected. All functions executed as and when required. The microcontroller master reset circuitry assured that the unit resets properly even when the voltage sags slowly.

The power supplies were loaded as designed during this time and found to be within 3% of the expected output. After the twelve-day test confirmed stability, the supplies were loaded with 2000% of the expected operating load. This represents the maximum load the regulators are capable of sustaining without generating a fault condition. The 3-V regulator proved to be exceptionally robust with an output ripple of less than 25 mV across the entire load range. The 9-V regulator was similarly robust but due to the boost switching topology generated up to 100 mV of ripple voltage under heavy loads or sudden load transitions and extremely high transients upon low voltage startup. This is not a concern in the current design since the 9-V regulator never starts up under heavy load. The sensors and conditioning circuitry draw less than 10 mA on startup.

Voltage regulators

The voltage regulators were loaded as designed during this time and found to be within 3% of the expected output. After the twelve-day test confirmed stability, the supplies were loaded with 2000% of the expected operating load. This represents the maximum load the regulators are capable of sustaining without generating a fault condition. The 3-V regulator proved to be exceptionally robust with an output ripple of less than 25 mV across the entire load range. The 9-V regulator was similarly robust but due to the boost switching topology generates up to 100 mV of ripple voltage under heavy loads or sudden load transitions and extremely high transients upon low voltage startup. This is not a concern in the current design since the 9-V regulator never starts up under heavy load. The sensors and conditioning circuitry draw less than 10 mA on startup.

Radio Interface

The radio system was tested for range of operation, power consumption, and link reliability. Range was tested by installing the unit in a typical monitoring environment and progressively putting more distance between the transmitter and receiver. The environment consisted of a local creek bed approximately eight feet below grade shadowed by low lying vegetation. The receiver was capable of picking up a signal from well over 200 feet with a partially submerged and non-optimally aligned antenna. This was foreseen to be a typical field condition and represents what would happen if the unit became inundated by the water body. Line-of-sight communications was tested with the transmitter and receiver placed on the same level with no intervening structures or obstacles. The range was found to be well over 500 feet with low gain antennas. Range can be further extended by better antenna selection and proper alignment.

Reliability of the RF link was tested by setting up the transmitter and receiver within the limits of the tested range then moving to the extreme limits while monitoring the data stream. It was found no appreciable amount of data was lost when within the tested range. When at the extreme limits of the range approximately 30% of the data was lost. It was of interest to identify the receiver behavior when the unit was taken outside of the reception range and then moved back into the reception range. When outside the receiver generated no spurious data packets and automatically identified the incoming signal when moved back into range. As the unit enters the reception range spurious data can be generated as data are not always completely recovered but the data are usually easily identified.

Power consumption was found to be well within the design limits. The radio used no more power than specified by the manufacturer and is therefore suitable for this design.

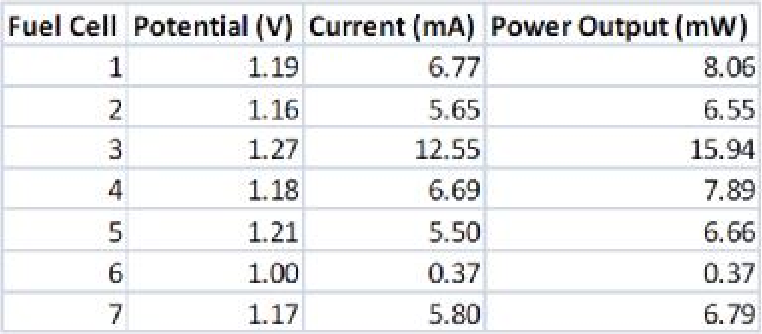
In Stage three, we also further tested the power supply (MFCs) both in the laboratory and in the field. Among the factors investigated were the effect of temperature on power output, the contribution of microbial action to the operation of the power supply, the performance of the power supply in a field environment, and the nature of the fluid flow through the membranes. Each property was researched individually in order to independently evaluate how it would affect the system as a whole. Through investigating these factors, a new design was proposed for the MFCs that would increase the power output. It was found that the power supply operated best in warmer environments with plenty of bacteria.

Figure 13. MFCs placed in the stream, featuring a simplistic enclosure.

Preliminary field test

Before the final field test, we preliminarily tested the first-generation microbial fuel cells at a creek field test site near WTI, as shown in Figure 13. The stream had a measured dissolved oxygen concentration of 9.07 ppm. The temperature of the stream was 15.2°C; the temperature of the water in the fuel cell container was 17.5°C. At the time measurements were taken, the air temperature was 15.6°C, with a slight breeze. The last rainfall was the previous night, and the flow rate was qualitatively judged to be moderate. The water sample had a pH of 8.55, which was expected because of the limestone surroundings. When we used the array of seven MFCs in series, it provided an output potential of 5.5 V in the absence of external load. The power outputs for the individual fuel cells are presented in Table 3, where the current was measured using a 100-Ω resistor as the external load.

Table 3. Performance of individual MFC during the preliminary field test



Fuel Cell	Potential (V)	Current (mA)	Power Output (mW)
1	1.19	6.77	8.06
2	1.16	5.65	6.55
3	1.27	12.55	15.94
4	1.18	6.69	7.89
5	1.21	5.50	6.66
6	1.00	0.37	0.37
7	1.17	5.80	6.79

When the fuel cell number 6 was excluded, the other six fuel cells had a potential of 6.7 V in series. Cell 6 was excluded because its power output was so low that it was limiting the system. The high voltage and current in the fuel cell number 3 likely indicate active contributions of manganese-oxidizing microorganisms to enhanced output potential and significantly reduced internal resistance of that specific fuel cell, whereas the low voltage and current in the fuel cell number 6 likely indicate the worst-case scenario where the fuel cell features little microbial activity and high internal resistance. The fuel cells were left in the stream, unconnected, for two weeks with regular monitoring. The fuel cells' outputs fluctuated but did not show any obvious decrease in power output.

During the preliminary field test, the MFC array was unable to provide enough power to sustain the function of the circuitry over a test period that included both temperature and sunlight fluctuations. Engineering improvements to be implemented may include: increasing the electrode surface area and reducing the internal resistance of the MFC array; improving the engineering design of the MFC array to minimize possible damage by silt. All electronics (signal conditioning circuits, microcontroller, and RF transceiver) were in working condition and performed as they should given how much power was being supplied. The microcontroller successfully executed the proper system functions based upon the measured output power of the MFC array. The sensor output was measured and verified to be within 10% of the actual parameter being tested, even though pH and chloride ion activity varied with the time of day as a function of water temperature. Further accuracy of these readings can be obtained by applying a compensation algorithm either in the firmware or on the PC.

Effect of water temperature of MFC performance

When the power supply was left in the sun to heat up, there was a noticeable increase in power output. The water temperature increased from 11.8°C to 13.8°C in a three-hour time span. After this increase in temperature, one out of eight fuel cells increased in potential and six out of eight increased in current. In terms of total power output, six out of eight fuel cells increased in power with the increase in water temperature, as seen in Figure 14.

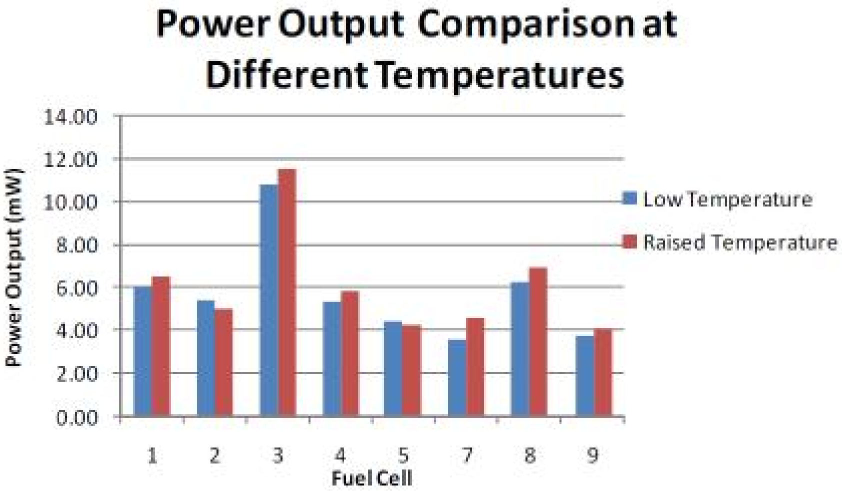


Figure 14. Effect of water temperature on the performance of individual MFC respectively.

When all eight fuel cells were connected in series, 6.03 V was produced at 11.8C. Once the final measurements were taken for the individual cells, the series voltage reading was taken every ten minutes for 30 minutes. These four readings were 6.14 V, 6.46 V, 6.42 V, and 6.38 V, respectively.

Membrane flow test

When the membranes were allowed to sit vertically with water in the polyvinylchloride (PVC) pipe, different flow rates were observed for the different membranes used in the array of MFCs. The anode and cathode membranes saw no flow through them, after they were left vertical for at least 24 hours. This was expected and means that the membranes are only exchanging ions. When the inner membrane was held vertically, water immediately began flowing through at a substantial rate. This leads to the conclusion that within the fuel cell water is flowing freely inside the cell without allowing water from the outside to flow into the chambers. This means that for the array of MFCs to be implemented in the field environment they do not need to be placed in a high flow area. Still or calm water will allow for ample ion exchange and the flow inside the cell is not dependent on the flow rate outside.

Battery Powered Field Test

Field demonstration was conducted in the Gallatin River watershed along U.S. Highway 191 just south of the MSU campus. This field testing location was specifically selected to be consistent with the requirements of the REU program, which was focused on various locations along U.S. 191 as it traversed the sensitive ecological system in southwest Montana’s Gallatin canyon. Two field test sites were chosen for validating the sensor performance (shown in Figure 16), where the electronics and sensor were implemented using the battery pack and the RF transceiver and laptop shown in Figure 15.

Figure 15. RF receiver and laptop used for the field test

Figure 16. Two battery powered test sites

During the field demonstration, the entire system was tested over the span of two weeks during varied weather conditions and functioned mostly as expected. The RF transmitter was tested to a maximum range of 250 meters with suboptimal antenna alignment due to the local terrain. Data (pH, chloride ion concentration, and temperature) was transmitted on a 60-second interval and proved to be within acceptable tolerances for the chosen sensors in the first 24 hours. By the end of two weeks, however, the field measurement of pH value for these sites were 5.94 and 6.76 respectively, which differed significantly from the pH value measured from the field-collected water samples (8.48), likely attributable to the organic matter buildup in the capillaries of the sensor bulb after two weeks of field exposure. When the system is actually implemented for field applications, a more robust, field-compatible sensor will be needed and a self-cleaning mechanism is highly desirable for long-term sensor reliability.

PLANS FOR IMPLEMENTATION

Through preliminary field testing, it was found that all electronics worked according to the design and the fuel cells' outputs fluctuated but did not show any obvious decrease in power output after two weeks of continuous immersion in a creek. Yet the first generation of fuel cells did not output sufficient power to run the sensors and power electronics. Improvements need to be made to further enhance the energy output by the MFCs, for instance, by increasing the electrode dimensions, by reducing the distance between cathode and anode, by improving the cathode design and surface treatment, and by improving the membrane materials to reduce internal resistance of MFCs. In addition, a more robust design is needed for the enclosure so that it can survive the high flow rate of the water in the field and avoid any possible damage by silt. We also anticipate the integration of the entire system into a compact package to be installed directly underneath a floatable platform on the surfacewater, such that it can work reliably independent of the water level.

Other improvements to be implemented in the next phase may include: incorporating other types of water quality sensors; enabling wireless communication of the near-real-time sensor data through the satellite and data presentation on the web; modifying the instrument pack to include a GPS transmitter and to include geo-tag and time stamp on the sensor data; procuring field-robust sensors and/or minimizing the buildup of algae on sensors to ensure long-term sensor reliability.

Nonetheless, the concept of using MFCs as a self-sustainable power supply was successfully demonstrated in this phase-one project. A key benefit of this technology is that the power supply is highly scalable and self-sustaining, as it can serve as a battery when there is no microbial activity and as a microbial fuel cell with enhanced energy output when there is microbial activity.

Once improved, this product will find potential applications in the highway environment, including but not limited to: early detection of toxins and pollutants in highway runoff at critical locations (such as the habitat for sensitive species); rapid measurements of environmental impacts of highway construction and operation on water quality; and evaluation of stormwater control facilities over time.

Extensive research has indicated the potential threat that highway runoff poses on the biological diversity and productivity of aquatic ecosystems (Staples et al., 2004). As a major source of the non-point source pollution, highway runoff has adverse effects on the adjacent aquatic resources if no measures are taken to remove the excessive contaminants accumulated from highway construction, operation and maintenance. Highway runoff often carries sediments, nutrients, heavy metals, petroleum-related compounds, deicers and other chemicals before it reaches the receiving water body. Compliance with water quality regulations along with a desire to minimize adverse environmental impacts have led to the need for deploying best management practices for highway runoff. As indicated by the U.S. Federal Highway Administration (TERP, 2005), “stormwater discharges from roads and highways represent an environmental issue requiring an understanding of … the relative contribution and magnitude of the environmental impacts on the ecological system". Similarly, the NCHRP IDEA program has idenfitied one of its focus areas as *Environment and Resource Conservation*, including "advanced monitoring methods to rapidly measure the environmental impacts of highway construction and operation". In addition, a recent NCHRP study has revealed that U.S. state departments of transportation

(DOTs) have the strongest needs and interests in the area of cost and performance of stormwater control facilities or BMPs (NCHRP, 2005).

While the current practice for water quality monitoring (i.e., manual data-collection) provides many environmental benefits, the proposed system has numerous additional advantages. First of all, the autonomous feature of the system minimizes the need for frequent manual sampling and testing, a time-consuming, costly, and sometimes dangerous task. Second, the self-sustainability of the system promises a reliable solution to long-term, wide-area monitoring of water quality along highways, as the system will demand minimum amount of maintenance or can operate in a reliable manner without any servicing. Third, the*in-situ* feasture of the system will enable near-real-time monitoring of water quality, and minimize the possibility of missing short-lived events due to the need to collect water samples or to change batteries. Such near-real-time data on water quality at distributed locations along highways, transmitted via telecommunication, will enable state DOTs in early detection and prompt mitigation of toxins and pollutants in highway runoff. Finally, the system provides state DOTs an efficient tool to identify seasonal trends in selected parameters of water quality (such as chloride and sediment loadings) along highways, to assess the impact of various highway activities on the water quality, and to evaluate the performance of various highway-runoff BMPs over time. Deploying such systems at distributed locations of concern may require a relatively high capital investment; in the long run however, it should be more cost-effective than manual data-collection activities as it minimizes labor hours required for water quality monitoring.

The research team is in the process of filing a provisional patent to protect the intellectual properties generated from this project, and funding will be pursued in order to further improve the capability, performance, reliability and cost-competitiveness of this technology and to bring it to the marketplace and into practice. The research team will work closely with end users from the State DOTs, to identify user requirements for this sensing system and to identify areas for improvement, in order to deliver a system that truly meets the users' needs. In the next phase, we will refine the proof-of-concept system and then deliver the improved prototype to partners in the state DOTs for further evaluation by end users.

Furthermore, we anticipate much greater performance of this power supply once implemented in marine environments where the electric resistivity of the aqueous solution is much greater than that seen in streams we tested, leading to much lower internal resistance of MFCs. For instance, the seawater features an electrical conductivity at least 960 times as high as that of stream water (4.8 vs. 0.05 $S \cdot m^{-1}$) and one can expect the power output of MFCs to be at least 200 times higher in seawater than in stream water. As such, we have been communicating with some Department of Defense stakeholders to explore the possible applications of this technology in the marine environments.

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