

Field Experiments on Bioelectricity Production from Lake Sediment Using Microbial Fuel Cell Technology

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Since particular bacteria are able to oxidize organic matter under anaerobic conditions with concomitant electricity generation while an electrode is serving as an electron acceptor in a fuel cell environment, microbial fuel cells (MFCs) have recently received significant attention. Prototype sediment MFCs were placed in a shallow hypereutrophic lake and generated current for over six months. During the experimental period, a higher electrical current density with an average of 20.4 mA/m² was produced using electrodes with higher specific surface areas. Furthermore, parallel connection of sediment MFCs increased the current output. The results showed that current production was severely dependent on temperature and dissolved oxygen concentrations at the cathode. Other findings of this study include not only the direct coupling of current production with a decrease in the organic matter content of the sediment, as well as high positive redox potentials (> +120 mV vs. SHE) in the vicinity of the active anode as compared to sediments where electrodes were not embedded. This implies that the electrochemically active anode evidently acted as an alternative electron acceptor in the sediment, which likely decreased the activity of methanogens and improved the overall decrease in organic matter of sediment. Consequently, this study suggests that the sediment MFC could provide a means for the bioremediation of organic-rich sediment via anaerobic oxidation in conjunction with current production.

Key Words : Anaerobic oxidation, Lake sediment, Microbial fuel cell, Organic matter, Redox potential

Introduction

Harvesting energy from renewable sources in order to minimize negative environmental impacts is one of the most critical challenges facing contemporary society. An MFC is a device that converts chemical energy to electrical energy through the catalytic reaction of microorganisms.¹ Since it was reported that particular bacteria are capable of transferring electrons directly to an anode as the electron acceptor in the absence of exogenous mediators, the operation of a mediator-less MFC has become possible. This property has been reported in a number of bacteria including *Desulfohalobus propionicus*,² *Geobacter sulfurreducens*,³ *Rhodospirillum rubrum*,⁴ and *Shewanella putrefaciens*.⁵ In an MFC, protons and electrons are produced while organic substrate (fuel) is oxidized at the electrochemically active anode by the bacteria responsible for current production mentioned above. They are subsequently moved to the cathode through the proton exchange membrane and the external electrical circuit,⁶ respectively. In the meantime, reduction of oxidant (e.g. oxygen) and consumption of protons and electrons occur, forming water at the cathode. Unlike in chemical fuel cells, various organic substrates, organic wastes as well as biomass, can be used as fuel in an MFC,⁷ offering the double benefit of simultaneously treating organic wastes and harvesting electricity through anaerobic oxidation.

Although MFCs have become recognized as a promising technology for treating wastewater with concomitant electricity generation,^{8,9} its field implementation is at present distant due to issues including problems with scaling-up and insufficient power output. Based on the concept of MFCs, some noticeable technologies have been developed for monitoring water quality and harvesting electricity from marine sediment. By using an MFC-type biochemical oxygen demand (BOD) sensor showing a linear relationship between the current generated and the strength of wastewater, it has become possible to measure BOD in real-time, while the conventional test requires a five-day incubation period.¹¹ Also, Kim et al. have reported the application of an MFC for monitoring toxic substances (e.g., heavy metals and anthropogenic organic compound) in water.¹² Another interesting category of MFCs is to generate electricity from marine sediment to power sensors and telemetry devices in remote area.¹³⁻¹⁶

Organic-rich sediment in freshwater and marine environments can be considered an abundant potential source of renewable energy when MFCs can become capable of generating greater amounts of electricity than is currently possible. In addition, sediment with high organic content in ponds and lakes is perceived to be an environmentally undesirable solid waste due to it containing a range of pollutants, resulting in water-quality issues and even methane emission (a gas with 23 times the greenhouse impact as

CO₂) under ferric and sulfate-depleted conditions.^{17,18} The purpose of this study was to investigate current generation from lake sediment, thereby sets of sediment MFC were constructed and operated under field conditions. While monitoring current output, the effects of environmental factors (*e.g.*, temperature and dissolved oxygen (DO) concentration in the overlying water) on current generation were studied. Also, the feasibility of sediment MFC for supporting bioremediation in the field was roughly evaluated by measuring redox potential and the change in organic carbon content of sediments.

Experimental

Construction of sediment MFCs. A total of seven sediment MFCs were installed at Lake Ilgam, an artificial lake in the Seoul metropolitan area created in 1957. The lake is small and shallow, with a surface area of about 55,661 m², a mean depth of about 1.5 m, and a long hydraulic retention time of approximately 288 days. This lake is recharged by rainfall and groundwater pumped from nearby subway stations. In this study, two distinct types of graphite electrodes, plate (IG-11, Toyo Tanso Co., Ltd., Osaka, Japan) and felt (SG-221, DONAC Co., Ltd., Osaka, Japan) were used. The surface of each type of electrode was viewed using scanning electron microscopy (SEM) (Fig. 1). Each plate-type electrode had a width of 100 cm, length of 50 cm, and thickness of 1.5 cm. A total of 120 holes with a diameter of 1 cm were drilled in the plate-type electrode. The apparent surface size of the felt-type electrode was 70 cm × 70 cm and its thickness was 1 cm. An electrical connection was made between anode and cathode with PVC insulated copper wires and stainless screws. Each end of the wires was firmly adhered to a stainless screw by using a conductive silver epoxy (Altex Electronics, Ltd., TX, USA). All contact points were completely covered with insulating epoxy (Devcon, IL, USA). The anode buried about 5 cm below the sediment-water interface. The cathode was horizontally positioned about 80 cm above the sediment-water interface and 5-10

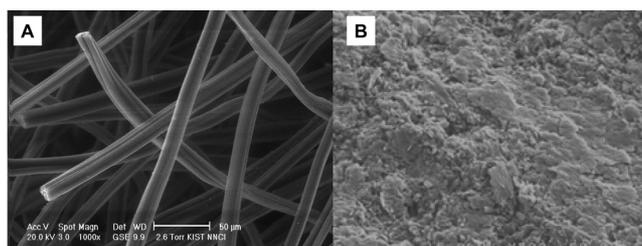


Figure 1. SEM images showing the surface of graphite felt (A) and plate electrode (B).

cm below the water surface. In the same manner as described above for an MFC, on the anode of sediment MFCs, non-fermentable organic matter (*e.g.*, acetate) produced by indigenous microorganisms is oxidized through the catalytic reaction of microorganisms including direct electron transfer to the electrode.¹⁹ Simultaneously, the reduction of oxygen available in the overlying water column takes place on the cathode (Fig. 2). Unlike a typical MFC, no proton exchange membrane is needed since a natural oxygen gradient exists across the sediment-water interface.

Operation of sediment MFCs. Sediment MFCs were operated for six months, including winter, in the year 2007. At the beginning of the experimental period, each sediment MFC was maintained under open-circuit conditions. A week later, the external resistance was switched to 10 Ω and sustained throughout the operating period. As shown in the above Figure 2, the closed-circuit potential between anode and cathode across a resistor was measured using a multimeter (Keithley Instruments, OH, USA) and recorded on a personal computer via an interface card (GPIB Interface Boards, Keithley). The current can be calculated from the measured voltage using Ohm's law as:

$$I = V/R \quad (1)$$

where *I* represents the current in amperes, *V* represents the potential difference between two electrodes in volts, and *R* represents the resistance measured in ohms. The current (power) density was calculated by dividing the current

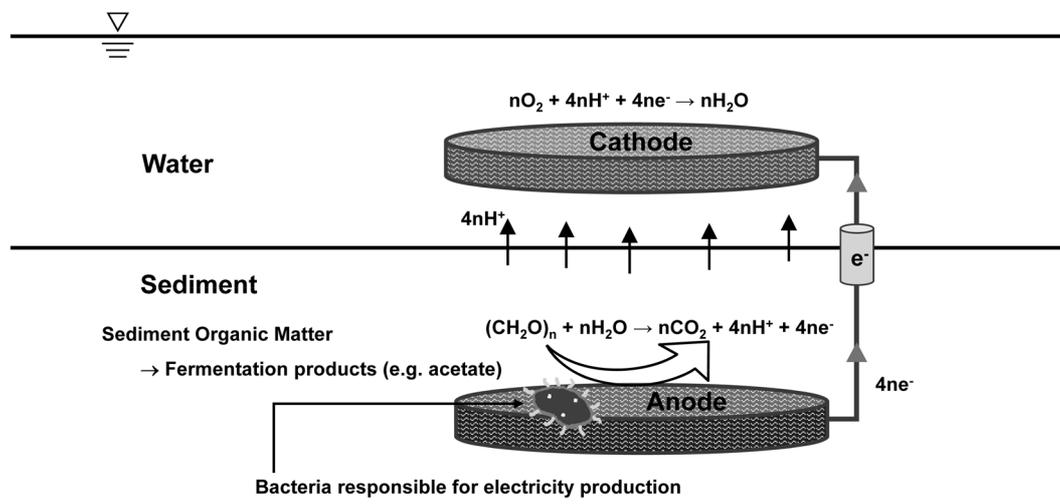


Figure 2. Schematic diagram of the sediment MFC embedded in the lake.

(power) by the apparent surface area of each electrode.

Analyses. In order to measure the amount of organic matter in sediments, loss on ignition (LOI) and readily oxidizable organic matter (ROOM) were determined. LOI is a simple, commonly used method for estimating the organic content of sediment. Organic matter is oxidized at 500-550 °C into carbon dioxide and ash. The LOI is then calculated as in the following equation (2):

$$\text{LOI}_{550} = ((\text{DW}_{105} - \text{DW}_{550}) / \text{DW}_{105}) \cdot 100 \quad (2)$$

where LOI_{550} is LOI at 550 °C as a percentage, DW_{105} is the dry weight in grams of the sample heated at 105 °C overnight, and DW_{550} is the dry weight of the sample in grams after being held for four hours at 550 °C. Before being weighed, all samples were cooled to room temperature in a desiccator.

In addition, ROOM in the sediment samples was determined through the Walkley-Black method (chromic acid method) as modified by Loring and Rantala.²⁰ This method is able to differentiate humic matter from extraneous sources of organic carbon (*e.g.*, coal and graphite) in sediment. All reagents used in this experiment were purchased from Sigma-Aldrich Korea, Ltd. The pH, DO, and conductivity were measured by using probes (Thermo Orion, MA, USA) connected to a portable multimeter (Star series, Orion). Also, the sediment redox potentials were measured by inserting an ORP (oxidation-reduction potential) electrode (9678 BNWP, Thermo Orion), previously calibrated with ORP standard (Cat. No. 900011) directly into the benthic sediment of the lake.

Results and Discussion

Effect of electrode type on current production. After the installation of sediment MFCs in the lake, they were operated under open-circuit conditions for one week. As shown in Figure 3A, the voltage increased gradually to 0.5 V within the first two days and remained above 0.5 V for the next few days. During this period, similarly increasing trends and voltage levels were observed from both sediment MFCs using different types of electrodes: the sediment MFCs using graphite felt as electrodes created a slightly higher output voltage.

After one week, the sediment MFCs were switched to closed-circuit conditions with an external load resistance of 10 Ω. Immediately after switching to closed-circuit conditions, a higher current density (*ca.* 10 mA/m²) was produced by sediment MFCs with porous graphite felt electrodes as compared with that with non-porous graphite plate (*ca.* 3 mA/m²). Electrical currents generated by each type of sediment MFCs gradually increased over the next few days (data not shown). After these periods, currents were generated at a relatively steady level for an additional six months (from May to October 2007). Throughout this experimental period, current generated from the sediment MFCs with porous electrodes was about four times higher than that from sediment MFCs with plate electrodes (Fig. 3B). It is strongly

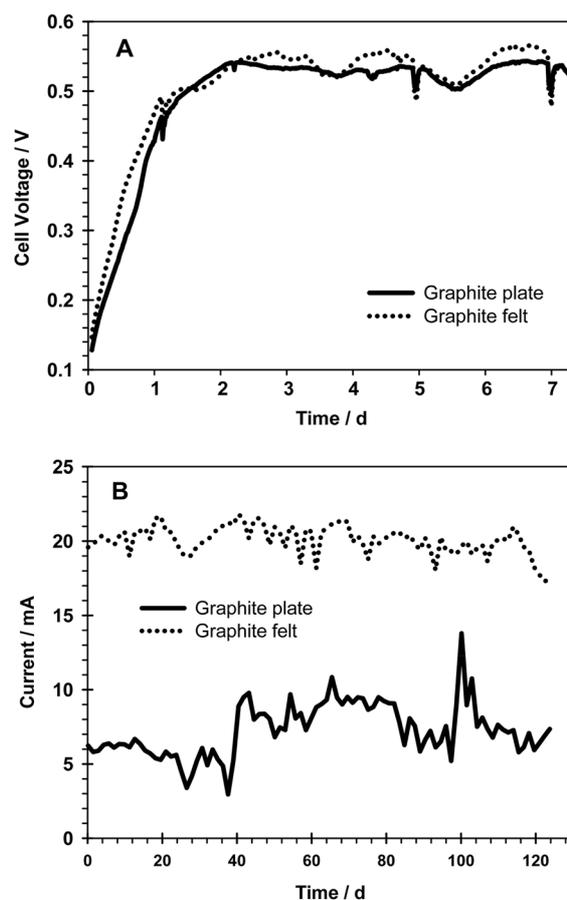


Figure 3. Voltage generation at the initial stage of operation under open-circuit conditions (A) and current production from sediment MFCs using two different types of electrodes under closed-circuit conditions (B).

believed that higher current production could be due to a result of the increased surface area for the growth of the bacteria that are responsible for electricity generation.

The power density of the sediment MFC can be calculated by dividing the power by the apparent surface area of the anode. During this period, the average current produced by sediment MFCs with graphite felt electrode was about 20 mA, equivalent to 4.08 mW m⁻². This value is dramatically lower (about 1/7-1/8) than the power density generated in marine environments.^{14,15} This could be due to several factors. Firstly, seawater has a higher electrical conductivity than freshwater: the conductivity of seawater and river water is about 50,000 and 500 μS cm⁻¹ at 20 °C, respectively.²¹ In MFCs, the internal resistance related to the conductivity of electrolyte is one of the more important factors affecting the high-power density performance.²² Thus, the increased internal resistance due to poor conductivity contributed to the decrease in power output since the average value of the conductivity measured at this site was 385 μS cm⁻¹. Additionally, other possible factors which can adversely affect the performance of sediment MFCs could include the organic carbon content of sediment, the rate of fuel oxidation and the distance between the two electrodes.

Current production by connecting sediment MFCs in

parallel. In order to produce greater current and power output, MFCs can be connected in parallel and series. Aelterman *et al.* reported that an MFC stack connecting six individual MFCs in series and parallel was able to produce high power densities at increased voltages or current with continuous feeding of acetate-based artificial wastewater, creating a higher current through parallel connection and a higher voltage through series connection.²³ Figure 4 shows the output current from two sediment MFCs connected in parallel. As observed in the operation of a single unit of sediment MFCs, a higher current was produced from sediment MFCs with felt type electrodes than from those with plate-type electrodes in this case. In this experiment, on the average, the current of two sediment MFCs connected in parallel was about twice as high as that of an individual. The fluctuation of current output would be due to changes in the oxygen availability at the cathode as described below. However, there was no significant voltage increase from sediment MFCs with felt and plate-type electrodes when two or more individual sediment MFCs were connected in series (data not shown). It may be speculated that the anodes of each sediment MFC were not completely and electrically isolated from one another because they were placed too close to each other in the sediment resulting in short-circuit current flow (the distance between two anodes was *ca.* 50 cm). Although the power from the sediment is not actually sufficient for the continuous operation of remote electronic monitoring devices, a capacitor electrically coupled to the sediment MFCs in parallel and capable of storing the energy generated could provide a solution to this issue.²⁴

Effect of environmental factors on current production.

Vertical variations of DO concentration in the lake at different times (morning, afternoon and evening) during the summer season are plotted in Figure 5A. DO concentration varied over time throughout the measurement period, ranging from 8 to 10 mg O₂ L⁻¹ near the water surface, where cathodes were positioned, in the afternoon, but decreasing to below 4 mg O₂ L⁻¹ in the morning. This small shallow lake is hypereutrophic, thereby increasing DO concentration at the surface during the daytime due to accelerated algal growth. DO concentration decreased significantly by the depth of the lake: the measured DO concentration approached zero at the sediment-water interface.

In MFCs, oxygen is widely used as the electron acceptor for the cathodic reaction due to its high redox potential. The reduction rate of oxygen at the cathode is considered to be among the limiting factors in the performance of MFCs.²⁵ Due to its poor catalytic activity, the cathodic reaction in the use of raw graphite is highly retarded when DO concentration is lower than 6.6 mg O₂ L⁻¹.^{26,27} As shown in Figure 5B, the amount of current output from sediment MFCs was found to be closely related to DO concentration at the cathode. The current production decreased abruptly when DO concentration fell lower than 5 mg O₂ L⁻¹. This result implies that the distance between two electrodes and DO concentrations available at the cathode are among several limiting factors to be thoroughly considered together when

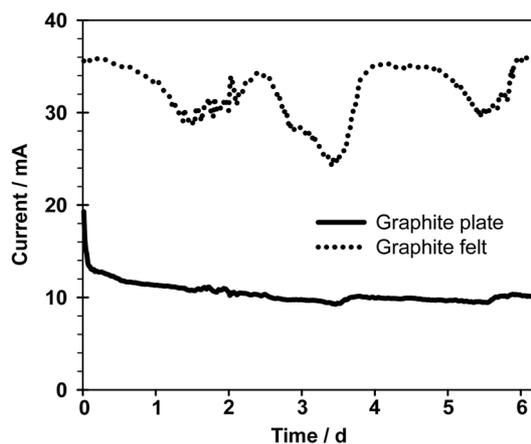


Figure 4. Current production by connecting two sediment MFCs in parallel.

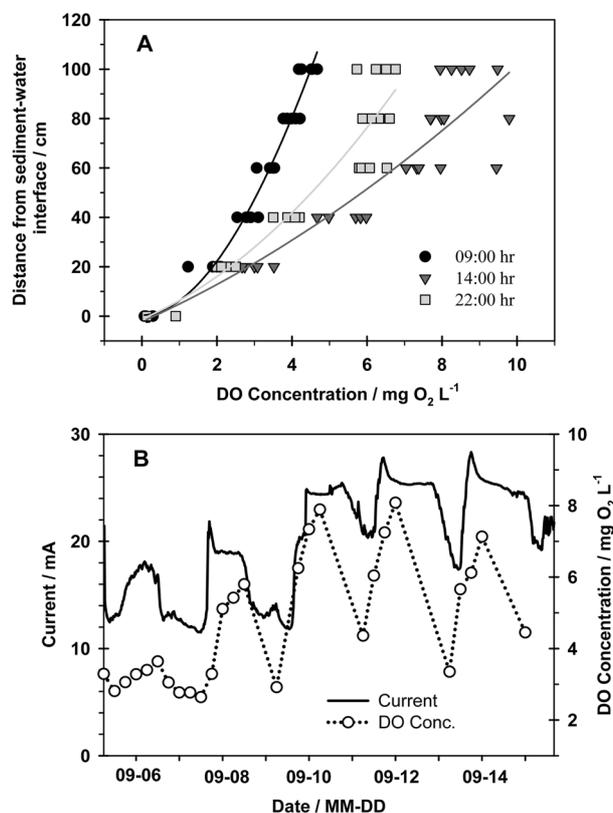


Figure 5. Vertical variations of DO concentration in the Lake at different times (A) and relation between DO concentration and current production from sediment MFCs (B).

operating sediment MFCs in field conditions. The cathode must be positioned close to the anode but levels of DO substantially higher than 5 mg O₂ L⁻¹ near the cathode are recommended.

Figure 6 shows the current output from sediment MFCs using graphite felt as electrodes during the winter season when sediment temperature ranged from 10 to 13 °C. Compared to the currents during the spring and summer (Fig. 3B), the current production decreased markedly, by more than one-half. Since DO concentration at the cathode was

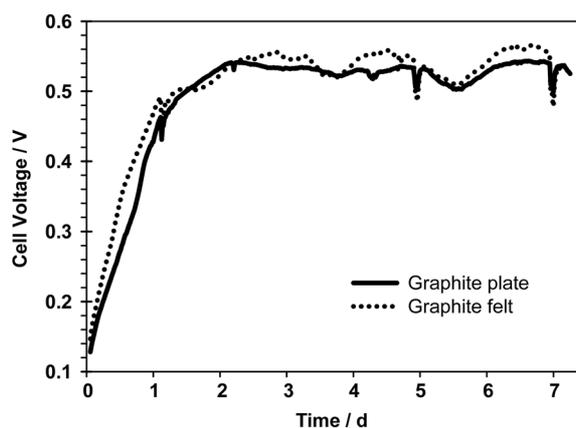


Figure 6. Current production from sediment MFCs with graphite felt electrodes during the cold winter season.

continuously maintained in the range of 6 to 7 mg O₂ L⁻¹ even during the cold season, this would indicate that the activity of bacteria responsible for electricity generation is markedly decreased owing to lower temperature in the sediment.

Throughout the experimental period, the pH of the overlying water ranged from 7.5 to 9.0 and no significant relationship between the pH and the current output was observed.

Changes in sediment under closed-circuit conditions. In order to assess the feasibility of the sediment MFC as a means for in-situ bioremediation of organic matter in subsurface environment while generating electricity, the organic content and redox potential of the sediment samples at different locations were measured. In the absence of oxygen, anaerobes are able to oxidize organic compounds (electron donor) in environments where electron acceptors such as nitrate, ferric oxides and sulfate are available.²⁸ Bond *et al.* reported that benzoate was completely oxidized to carbon dioxide in an MFC environment while 84% of the electrons extracted from benzoate oxidation were retrieved by the electrode.²⁹ As presented in Table 1, the direct coupling of current production with a decrease in the organic matter in the sediment at the active anode area was observed from the sediment MFC (with graphite felt electrodes) operated for six months. Under closed-circuit conditions, sediment organic matter content in terms of LOI and ROOM decreased by 21.9 and 32.7%, respectively, throughout the experimental period. In contrast, no decrease (a slight increase) in organic content was observed from the sediment where the electrodes were not placed. This verifies that the anode served as an alternative electron acceptor in the presence of biodegradable organic matter in sediment under electricity generating conditions.

More interestingly, a tremendous difference for the redox values of the sediment amended with and without the electrodes was observed: distinctly positive redox potentials near the anode area in sediment MFCs operated under closed-circuit conditions may indicate that the growth of methane producing bacteria can be inhibited. Because sulfidogenesis

Table 1. Changes of organic matter content and redox potential of sediment samples

	LOI (%)	ROOM (%)	Eh (mV, vs SHE)
Initial sediment samples	10.4 ± 0.31	3.52 ± 0.38	–
Sediment near active anode	8.12 ± 0.17	2.37 ± 0.23	+128 ± 37
Sediment not amended with electrodes	10.9 ± 0.15	3.26 ± 0.27	-152 ± 45

All measurements were performed on triplicate samples (Mean ± standard deviation).

and methanogenesis can be initiated under strongly reducing environments wherein the redox potential falls below approximately -100 mV.^{30,31} Thus, it has been shown that raising the redox potential of environments leads to a substantial decrease in methanogenic activity.³² Conversely, the redox potential of the sediment where electrodes were not installed was lower than -150 mV (vs. SHE), indicating that the sediment was quite reduced. This may allow the production of methane as well as hydrogen sulfide because methanogenesis is responsible for the majority of the terminal carbon metabolism in freshwater sediments under anaerobic conditions.³³ Although methane production was not directly measured in this study, Ishii *et al.* recently reported that it was suppressed in a laboratory-scale MFC inoculated with rice paddy soil and fed cellulose as a fuel under current generating conditions, while methane was produced under no-current conditions.³⁴ Consequently, it is plausible that the active anode in sediment MFCs has contributed to increasing the redox potential of sediment, potentially leading to suppression of methanogenic activity.

Conclusions

In this field study, the amount of current output was dependant upon DO concentration available at the cathode and upon temperature. If graphite is used without any modification it is recommended to position the cathode as close to the anode as possible where the level of DO concentration is higher than 5 mg O₂ L⁻¹. In terms of current density, improved performance of sediment MFCs was achieved by utilizing electrodes with higher specific surface areas and connecting two of them in parallel. It is also noteworthy that embedding the electrode into sediment and completing the circuit has decreased the organic matter content of the sediment and increased sediment redox potential to positive values too high for methanogenesis. Thus, sediment MFCs have the potential to be explored as a means for bioremediation of organic-rich sediments, such as rice paddy fields, wetlands, and other contaminated subsurface environments. In order to expand their potential applications in environments, further studies are required to increase current production through minimizing the factors limiting the performance of sediment MFCs and to determine the fate of other pollutants (*e.g.*, heavy metals) in sediments.

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