

Mercury Detection Utilizing an Aquatic Animal as a Remote- Sensing Platform

August 2024

Jun Lu
Jian Liu
Wonseop Hwang
Jayson Martinez
Huidong Li
Daniel Deng

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Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

Mercury species in open water, especially the accumulated methylmercury ion, pose a threat to fish and environment. Therefore, it is important to develop a small sensor package that can be integrated into a biotelemetry sensor carried by an aquatic animal, enhancing the ability to detect mercury contamination in large water areas. A quartz crystal microbalance (QCM) sensor using metal-organic framework (MOF) as sensing material was developed to detect mercury and methylmercury ions in real time based on acoustic wave perturbation. Thiol groups were introduced into the MOF UiO-66 through the organic linker to prepare the UiO-66-SH which was confirmed by infrared spectroscopy results. Batch adsorption experiments were conducted for the Hg^{2+} , CH_3Hg^+ , and Ca^{2+} ions adsorption in the UiO-66-SH. The adsorption capacities of the mercury ions were more than an order of magnitude higher than those of the competing Ca^{2+} ions at the same concentration. The frequency changes of the QCM sensor with the UiO-66-SH sensing film were an order of magnitude higher than those of the controlled baseline QCM sensor without a sensing film. Additionally, the frequency change can be tailored by adjusting the thickness of the MOF film and the adsorption properties of the sensing material. The sensor frequency change correlates well with ion adsorption capacities.

Acknowledgments

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Acronyms and Abbreviations

AAS	atomic-absorption spectrophotometry
AFS	atomic fluorescence spectrometry
BET	Brunauer-Emmett-Teller
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
LIBS	laser-induced breakdown spectroscopy
MOF	metal-organic framework
SAW	surface acoustic wave
QCM	quartz crystal microbalance
XRF	X-ray fluorescence spectrometry

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1.0 Introduction

Mercury is one of the most serious contaminants threatening our Nation's waters because it is a potential neurological poison in fish, wildlife, and humans. Many rivers and lakes are contaminated with mercury at concentrations that can exceed thresholds for hazardous waste¹. The most common form of bioaccumulation is methylmercury (CH_3Hg^+), which accounts for more than 95% of the accumulated mercury.² High levels of mercury can also have negative effects throughout the food chain. It is time-consuming and expensive to conduct measurements for mercury contamination in river and lake environments with conventional manual water sampling and lab testing, particularly given the large spatial volume involved.

Cold-vapor atomic-absorption spectrophotometry (AAS) is considered state-of-art technology for quantifying mercury in water. In which mercury samples are extracted and preconcentrated before being sent to the light path for measurement.³ The AAS method was selected by the United States Environmental Protection Agency for preparation and analysis of water samples for compounds containing mercury.⁴ The detection limit varies from $\mu\text{g/L}$ to ng/L depending on the size of the collected mercury sample in water. Many other analytical methods including atomic fluorescence spectrometry (AFS),⁵ inductively coupled plasma optical emission spectrometry (ICP-OES),⁶ inductively coupled plasma mass spectrometry (ICP-MS),⁷ laser-induced breakdown spectroscopy (LIBS),⁸ X-ray fluorescence spectrometry (XRF)⁹ and optical emission spectrometry¹⁰ have been studied for Hg determination.

Despite their high sensitivities, all these approaches require transportation of samples, sophisticated chemistry, expensive instruments, and up to a week to obtain non-real-time results. Moreover, some of these methods lack sufficient sensitivity for detecting CH_3Hg^+ .¹¹ We aim to develop alternative sensing technology that is cost-effective and capable of detecting low concentration of CH_3Hg^+ in water in real-time. Preliminary investigations of mercury sensing methods indicate that carbon paste electrode and Surface Acoustic Wave (SAW) sensor show promise as sensing platforms for mercury detection in tagged aquatic animals.^{12,13} PNNL has developed a carbon paste electrode for mercury detection⁵ and has a strong background in SAW sensing technology. However, significant effort is required to demonstrate the feasibility of selectively detecting mercury ions in water and explore pathways to integrate mercury sensing with biotelemetry technologies to potentially monitor mercury in situ and in real-time.

One alternative economical method is to integrate real-time mercury detection technology into a biotelemetry sensor that can be carried by an aquatic animal. The Lab-on-a-Fish developed at PNNL recently is the world's first biotelemetry sensor that combines cutting-edge computing with wireless sensing of in vivo physiology, behavior, and ambient environment.¹⁴ The Lab-on-a-Fish sensor can continuously operate for up to eight months. Thus, a similar biotelemetry device for detecting mercury could provide unprecedented capabilities for sensing mercury over large spatial volumes as the animal moves through its natural environment. Because Lab-on-a-Fish can also provide the 3D locations of the tagged aquatic animal, the proposed device would also function as an autonomous mobile sensor, associating mercury readings with specific water locations. Using fish as a remote-sensing platform for identifying hotspots of mercury contamination could result in substantial cost savings compared to labor-intensive, large scale monitoring campaigns conducted by workers in boats.

2.0 Material Preparation and Characterization

We proposed of using acoustic wave sensor, such as SAW and QCM, with MOF as the sensing material for detecting Hg species. Thiol group, known for their strongly bind with Hg ions and other heavy metals, were introduced into the linker of a Zr-based MOF to achieve a potential high loading density thanks to the high surface area of the MOF (Figure 1).^{15,16} The Zr-MOF has good hydrothermal stability, which is important for the application of Hg ion detection in water.

The QCM sensor is a well-established and sensitive technique used to measure the interactions of molecules with a sensor surface, in air or liquid and in real time. It operates based on change in the resonant frequency of a quartz crystal sensor when it is covered with a thin film or liquid. The frequency change is used to determine the hydrated mass coupled to the sensor surface, with sensitivity in the ng/cm^2 range and thicknesses of nm to μm . The frequency change of the QCM sensor can be correlated with the mass change resulting from the ion species adsorption on the MOF sensing film.¹⁷

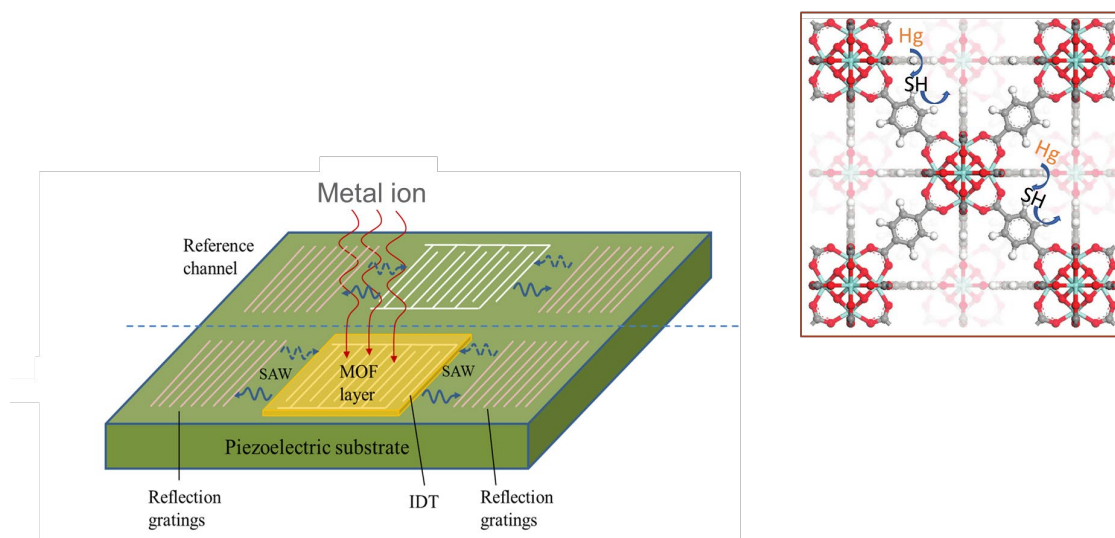


Figure 1. Acoustic wave sensor for mercury ions detection using MOF with thiol groups (UiO-66-SH) as the sensing material.

2.1 Thiol Functional Group

The Zr-MOF with thiol group (UiO-66-SH) was synthesized following the literature procedure and the Zr-MOF without thiol group (UiO-66) was also synthesized for comparison purpose.¹⁸ For the synthesis of UiO-66-SH, the synthesis procedure was similar to that of the UiO-66 except that the linker was replaced by 2,5-dimercaptoterephthalic acid ($\text{H}_2\text{BDC}-2,5\text{SH}$). The X-ray diffraction patterns for these two MOFs were shown in Figure 2a. The introduction of thiol group to the organic linker did not change the crystal structure of the MOF but reduce the crystallinity from the decreasing of the peak intensity for the UiO-66-SH. The thiol group in the UiO-66-SH was also confirmed using the FT-IR and the characteristic peak of thiol was identified at 2567 cm^{-1} (Figure 2b).¹⁹

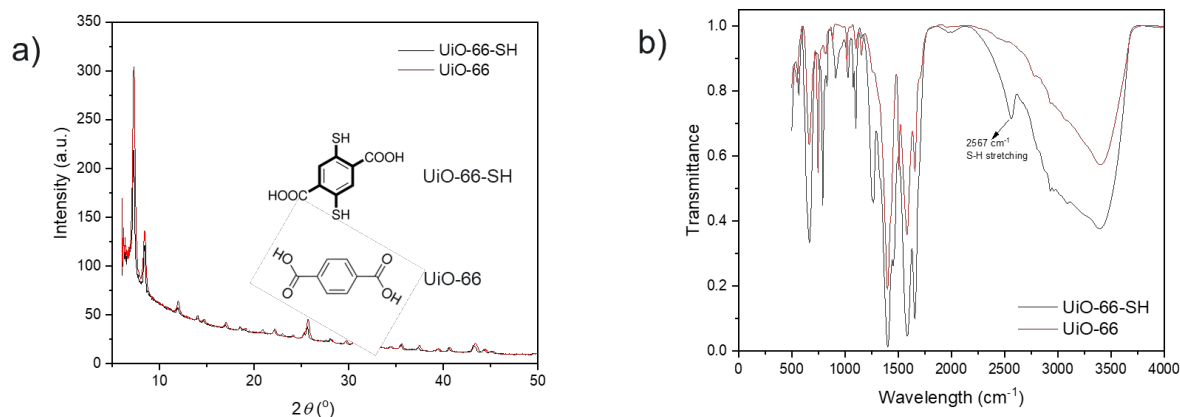


Figure 2. a) XRD and b) FT-IR results comparison for MOF materials.

2.2 Surface Area

The Brunauer-Emmett-Teller (BET) surface areas for both MOFs were measured using N_2 adsorption at 77K and the results are shown in Figure 3a and 3b for the UiO-66-SH and UiO-66, respectively. The BET was used to measure the specific surface area of materials, which is an important factor in understanding their physical and chemical properties. The UiO-66 had a higher surface area at $990\text{ m}^2/\text{g}$ than that of the UiO-66-SH ($306\text{ m}^2/\text{g}$).

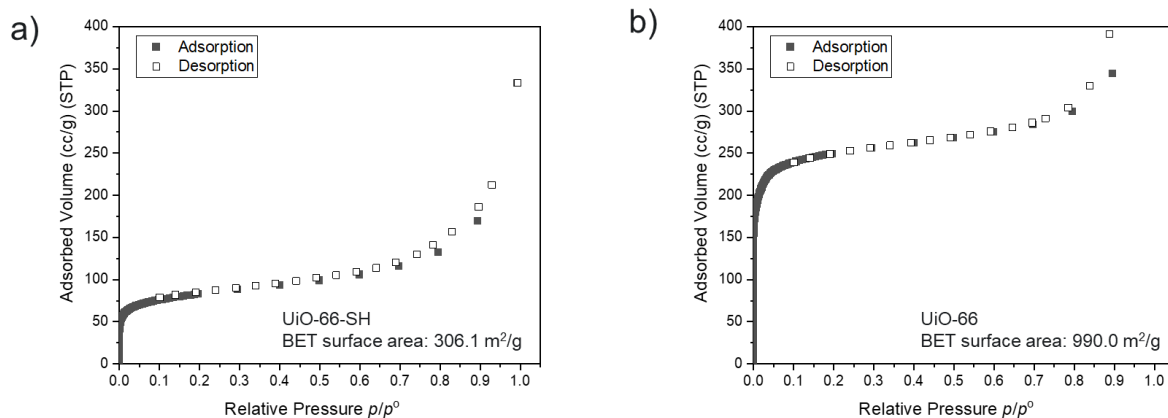


Figure 3. BET surface area results for MOF materials. a) UiO-66-SH; b) UiO-66.

2.3 Batch Adsorption of Metal Ions

The adsorption isotherm equilibrium and kinetics of various ions in MOFs were tested in the batch adsorption experiment. The UiO-66-SH was tested for all Hg^{2+} , CH_3Hg^+ , and Ca^{2+} adsorption in water. In a typical isotherm measurement, 10 mg of MOF sample was put inside of a tube with 10-40 ml solutions with different concentrations (5 - 200 ppm) of metal ions. Then the tubes were put in a shaking bed to facilitate the adsorption equilibrium for 24 h. After this,

the upper liquid after centrifuge was sampled to quantify the ion concentration after adsorption using analytical method. The adsorption capacity was then calculated based on the change of the ion concentration before and after adsorption and the mass of the MOF sample.

All the adsorption isotherms were fitted by the Freundlich model. It is evident that the adsorption of Hg^{2+} and CH_3Hg^+ was much stronger than that of the Ca^{2+} , as indicated by the difference in the adsorption capacities at the same concentration (Figure 4). The adsorption isotherm was steeper at the low concentration (below 5 ppm) for Hg^{2+} compared to CH_3Hg^+ adsorption in the UiO-66-SH. On the other hand, the adsorption of Hg^{2+} was so low in the UiO-66 that the adsorption loadings could not be estimated based on the ICP-OES results.

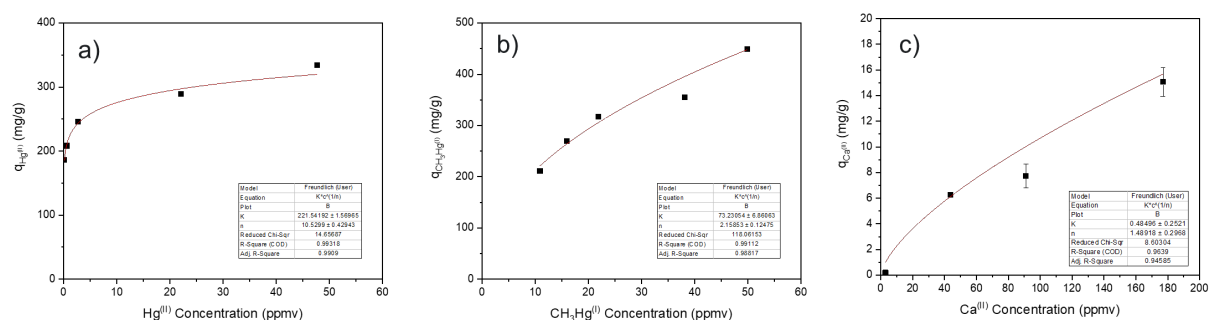


Figure 4. Adsorption isotherms at room temperature for three metal ions in UiO-66-SH. a) adsorption isotherm for Hg^{2+} ; b) adsorption isotherm for CH_3Hg^+ ; c) adsorption isotherm for Ca^{2+} .

The adsorption kinetic results for Hg^{2+} adsorption in the UiO-66-SH are shown in Figure 5a and the fitting results using the pseudo-first-order and the pseudo-second-order models are shown in Figure 5b and 5c, respectively. The adsorption of Hg^{2+} increased with time and reached equilibrium after 24 hours. The adsorption kinetic of Hg^{2+} fitted better with the pseudo-second-order model, as evidenced by higher correlation coefficients compared to the pseudo-first-order model. This indicates that the adsorption of Hg^{2+} in the UiO-66-SH was proportional to the adsorption site.²⁰

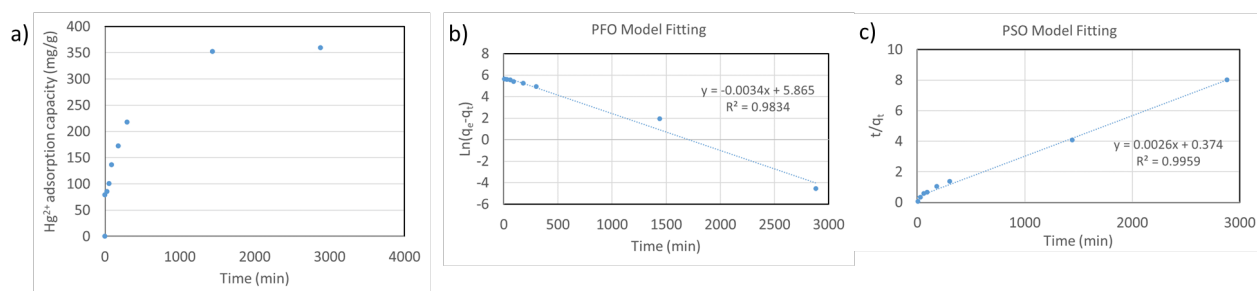


Figure 5. Adsorption kinetics for Hg^{2+} adsorption in the UiO-66-SH. a) Hg^{2+} adsorption loading change with time; b) Fitting of pseudo-first-order model; c) Fitting of pseudo-second-order model.

3.0 Sensor Test Results

A MOF-based QCM sensor was developed to detect different mercury species in situ and in real time. The competing Ca^{2+} was also tested to show the selectivity between mercury species and other co-existing ions in open water. The UiO-66-SH was dispersed in methanol (1g/L) with polyvinyl butyral (PVB, 0.2g/L) and spray coated on to a QCM sensor (5 MHz) using air brush method. Two sensors were made with 6-times coating and 12-times coatings. After air dry, the coated QCM sensor was put into the test instrument (X1 TCU, AW Sensors) and tested the frequency change at 23 °C with a sensor flow cell (Figure 6). The volume of the connection tube was small enough so that the flow time did not affect the sensor responding time.

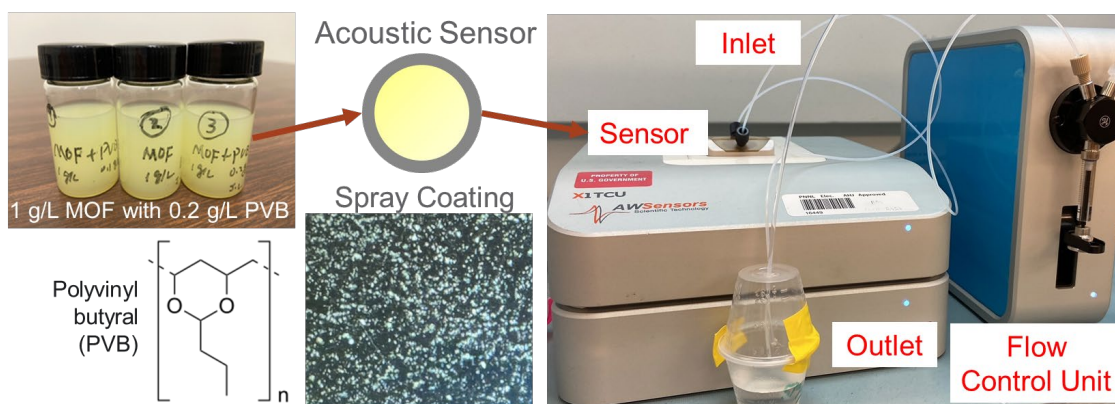


Figure 6. Sensor flow cell test system for metal ions in water.

3.1 QCM sensor results

The coated sensors were tested for the detection of 5 ppm and 50 ppm Hg^{2+} ion in water. The frequency of the coated QCM sensor in DI water (0 ppm Hg^{2+}) was used as the baseline, which was used to subtract the signals obtained with Hg^{2+} in water (Figure 7a). Frequency was recorded every 10 min after the change of concentration of Hg^{2+} . It is evident that the coated QCM sensor showed much larger frequency change compared to the non-coated one. This result confirmed that MOF with large surface area and selective thiol adsorption sites can effectively detect mercury species in water. The frequency change was larger at 50 ppm Hg^{2+} compared to 5 ppm Hg^{2+} , which is consistent with the isotherm trend. Additionally, the frequency change was larger with more coatings, indicating that it is possible to achieve lower detection limit with higher loadings of MOFs. Because the loadings are in μg per sensor, so the cost of the MOF material will not become an issue even at the current premiere price. The frequency change for Hg^{2+} is higher than that of the CH_3Hg^+ at the same concentration (Figure 7b,). Although we expected to observe larger frequency change due to the higher loading of CH_3Hg^+ , the frequency change was recorded smaller compared with that of the Hg^{2+} due to the slow adsorption of the much larger CH_3Hg^+ ions. The frequency change for Hg^{2+} is much higher than that for Ca^{2+} (Figure 7c), indicating selective detection of Hg^{2+} , which is consistent with the adsorption isotherm results.

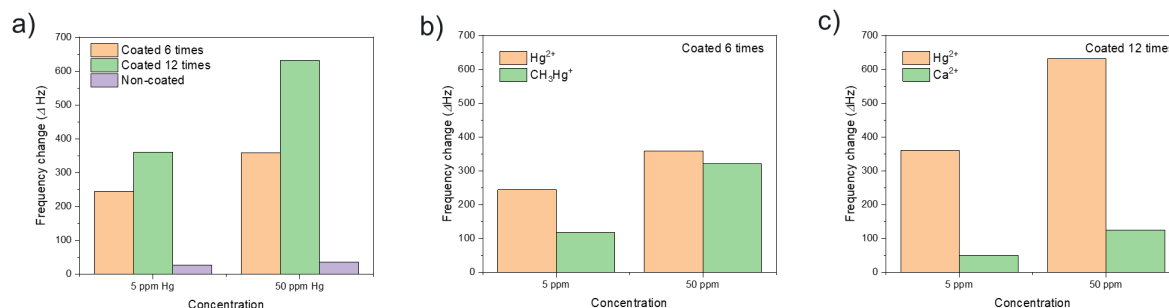


Figure 7. Coated QCM sensor frequency change comparison. a) the coating thickness effect; b) comparison between Hg^{2+} and CH_3Hg^+ ; c) comparison between Hg^{2+} and Ca^{2+} .

Table 1 shows the summary of the test results for coated QCM sensors. The QCM sensor samples were named by the coating layer of the UiO-66-SH and the test targets. UiO66SH_0_Hg indicates that this sample sensor was tested for Hg^{2+} adsorption and with no coating of UiO66SH coating. UiO66SH_6_Hg means that the sample sensor was tested for Hg^{2+} adsorption and with 6 layers coating of UiO66SH. UiO66SH_12_Hg is for the sample sensor that has 12 layers coatings and used to detect Hg^{2+} . UiO66SH_6_CH3Hg means that the sample sensor was tested for CH_3Hg^+ adsorption and with 6 layers coating of UiO66SH. UiO66SH_12_Ca means that the sample sensor was tested for Ca^{2+} adsorption and with 12 layers coating of UiO66SH. The frequency change observed here is on the same order of magnitude (about 60%) for the frequency change calculated based on the adsorption loadings in the isotherm. These results proved that it is possible to develop an economic QCM sensor with selective adsorption of mercury species and can be used to detect them in situ and in real time.

Table 1. Summary of the results for coated QCM sensors.

Sample	Metal Ion	Conc. (ppm)	Coated Layer	ΔF (Hz)
UiO66SH_0_Hg	Hg^{2+}	5	-	27
UiO66SH_0_Hg	Hg^{2+}	50	-	37
UiO66SH_6_Hg	Hg^{2+}	5	6	244
UiO66SH_6_Hg	Hg^{2+}	50	6	359
UiO66SH_12_Hg	Hg^{2+}	5	12	360
UiO66SH_12_Hg	Hg^{2+}	50	12	632
UiO66SH_6_CH3Hg	CH_3Hg^+	5	6	119
UiO66SH_6_CH3Hg	CH_3Hg^+	50	6	203
UiO66SH_12_Ca	Ca^{2+}	5	12	51
UiO66SH_12_Ca	Ca^{2+}	50	12	74

* All the frequency changes were obtained based on the baseline obtained in the DI water case.

4.0 Summary

In this LDRD project, we successfully developed a desktop QCM sensor prototype coated with the UiO-66-SH sensing material for detecting different ppm level concentrations of Hg^{2+} and CH_3Hg^+ ions in water. Increasing the mass of the MOF led to a larger frequency change of the sensor. The selective adsorption of UiO-66-SH MOF toward Hg^{2+} over Ca^{2+} was confirmed with both frequency changes and the adsorption batch experiment. It is possible to optimize the coating of the sensing film and material to demonstrate detection of Hg species at ppb level concentration. This project positions PNNL to potentially conduct underwater mercury detection studies using aquatic animals and established a foundation for sensing other chemicals because of the modular design of the proposed sensing system.

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Pacific Northwest National Laboratory

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