



## Spatial distribution of hydrogen sulfide and sulfur species in coastal marine sediments Hiroshima Bay, Japan

Satoshi Asaoka<sup>a,\*</sup>, Akira Umehara<sup>b</sup>, Sosuke Otani<sup>c</sup>, Naoki Fujii<sup>d</sup>, Tetsuji Okuda<sup>e</sup>, Satoshi Nakai<sup>f</sup>, Wataru Nishijima<sup>b</sup>, Koji Takeuchi<sup>g</sup>, Hiroshi Shibata<sup>g</sup>, Waqar Azeem Jadoon<sup>a</sup>, Shinjiro Hayakawa<sup>f</sup>

<sup>a</sup> Research Center for Inland Seas, Kobe University, 5-1-1 Fukaeminami, Higashinada, Kobe 658-0022, Japan

<sup>b</sup> Environmental Research and Management Center, Hiroshima University, 1-5-3, Kagamiyama, Higashihiroshima, Hiroshima 739-8513, Japan

<sup>c</sup> Department of Technological Systems, Osaka Prefecture University College of Technology, 26-12, Saiwaicho, Neyagawa, Osaka 572-8572, Japan

<sup>d</sup> Institute of Lowland and Marine Research, Saga University, 1, Honjyo, Saga 840-8502, Japan

<sup>e</sup> Faculty of Science & Technology, Ryukoku University, 1-5 Yokotani, Setaoe, Ootsu, Shiga 520-2194, Japan

<sup>f</sup> Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

<sup>g</sup> National Institute of Technology, Hiroshima College, 4272-1, Higashino, Oosakikamishima, Toyota, Hiroshima 725-0231, Japan

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### ABSTRACT

This study aims to reveal spatial distribution of hydrogen sulfide and sulfur species in marine sediments in Hiroshima Bay, Japan, by direct analyses using a combination of detection tubes and X-ray absorption fine structure spectroscopy. In summer and autumn, the hydrogen sulfide concentration ranged from  $< 0.1$  to  $4 \text{ mg-SL}^{-1}$ . In this study, only hydrogen sulfide was observed in autumn and at two stations in summer. In contrast, some earlier studies reported in all seasons in Hiroshima Bay the presence of acid volatile sulfide, which is used as a proxy of sulfide content. The sulfur species in sediments were mainly identified as sulfate, thiosulfate, elemental sulfur, and pyrite. Thiosulfate was a minor component compared to the other sulfur species. The formation of pyrite and sulfur derived from hydrogen sulfide oxidation played an important role in the scavenging of hydrogen sulfide.

### 1. Introduction

In enclosed water bodies such as inland seas, ports, and harbors, coastal marine sediments are affected by significant terrigenous organic matter loads. Thus, the high flux of organic matter leads to the rapid depletion of oxygen in the sediments due to intense microbial activity. Under such anoxic conditions, sulfate-reducing bacteria (SRB) utilize sulfate as a terminal electron acceptor for the degradation of organic matter and generates hydrogen sulfide (Muyzer and Stams, 2008). Hydrogen sulfide can also cause blue tide called ‘Aoshio’ (Otsubo et al., 1991), which is the formation of colloidal sulfur derived from the upwelling of hydrogen sulfide with anoxic bottom waters. This process consumes dissolved oxygen in the water column and gives off a bad odor. Approximately 27–50% of oxygen demand was oxidation of reduced species such as Mn(II), Fe(II),  $\text{H}_2\text{S}$  in Hiroshima Bay (Seiki et al., 1994; Yamamoto et al., 2011). Therefore, hydrogen sulfide is a significant contributor to the development of hypoxia. Additionally, hydrogen sulfide can cause serious problems for fisheries and benthic ecosystems because it is highly reactive and toxic. The toxicity of hydrogen sulfide for plants and aquatic organisms results from hydrogen

sulfide interfering with cytochrome *c* oxidase, the last enzyme of the electron transport system (Raven and Scrimgeour, 1997; Gray et al., 2002; Affonso et al., 2004; Lloyd, 2006; Dooley et al., 2013). Most aquatic organisms are negatively affected by hydrogen sulfide in the range of  $0.094$ – $1.9 \text{ mg-SL}^{-1}$  (Marumo and Yokota, 2012). Therefore, hydrogen sulfide has been generally detected and found to be a threat for benthic ecosystems in enclosed and/or semi-enclosed water bodies (Wang and Chapman, 1999; Caddy, 2000; Sakai et al., 2013; Yamamoto et al., 2015).

The sulfide contents including hydrogen sulfide in marine sediments have been conventionally evaluated by measuring acid volatile sulfide (AVS). This is a simple method by which hydrogen sulfide gas is released from sediments by the addition of acid (Rickard and Morse, 2005). Therefore, AVS is widely used in the fields of biogeochemistry, environmental science, and fisheries sciences (Jonge et al., 2010; Machado et al., 2010; Simpson et al., 2012; Gao et al., 2013; Arfaeina et al., 2016). However, AVS is operationally defined as a component of sedimentary sulfide (from both pore water and sediment) and potentially includes dissolved sulfur species, FeS clusters, iron sulfide nanoparticles, mackinawite (FeS), greigite ( $\text{Fe}_3\text{S}_4$ ), and pyrite ( $\text{FeS}_2$ ; Rickard

\* Corresponding author.

E-mail address: [s-asaoka@maritime.kobe-u.ac.jp](mailto:s-asaoka@maritime.kobe-u.ac.jp) (S. Asaoka).

and Morse, 2005). Therefore, AVS may exaggerate the hydrogen sulfide concentration and may detect hydrogen sulfide even if it is not present in the sediments (Fig. S1). In the case of sediments, sequential extraction is conventionally used to specify sulfur species (Nriagu and Soon, 1985; Rice et al., 1993; Thamdrup et al., 1994). In spite of their widespread use, there are concerns that sequential extractions might give misleading results because the method is complicated and time-consuming. For example, sequential extraction bears a high risk of misinterpretation due to the redistribution, readsorption, and oxidation of the analyte during the sequential extraction steps (Calmano et al., 2001). Therefore, it might not be appropriate to use sequential extraction to identify the sulfur species in marine sediments (Fig. S1). However, precisely identifying chemical species of sulfur in marine sediment is imperative for revealing the reductive and oxidative pathways of the sulfur cycle as well as the degradation of organic matter (Jørgensen and Kasten, 2006; Muyzer and Stams, 2008; Risgaard-Petersen et al., 2012; Pjevac et al., 2014; Markovic et al., 2015). To reliably determine the concentration of highly reactive and unstable hydrogen sulfide, rapid and on-site measurements were required. Previously, many methods such as spectrophotometric detection including the methylene blue method, the flow injection method, fluorimetric detection including a hydrogen sulfide sensor, 2-D hydrogen sulfide measurement, chemical probes, and gas chromatography were used to determine the hydrogen sulfide concentration (Cline, 1969; Kubáň et al., 1992; Radford and Cutter, 1993; Lawrence et al., 2000; Choi and Hawkins, 2003; Zhu and Aller, 2013; Li et al., 2013; Zhang and Guo, 2014). However, these methods are not always appropriate for on-site and rapid analyses. The concentrations of hydrogen sulfide in sediments were investigated in a hypersaline lake, a lagoon (Habicht and Canfield, 1997), brackish water basins (Scholz et al., 2013), brackish water bodies (Jørgensen, 1977), a coastal brackish lake (Sakai et al., 2013) and a eutrophic saline lake (Reese et al., 2008). However, field observations involving the direct determination of hydrogen sulfide in enclosed water bodies, especially those located adjacent to densely populated areas, are limited.

In this study, to overcome these problems, we used a detection tube and X-ray absorption fine structure (XAFS) spectroscopy. The detection tube can measure the concentration of hydrogen sulfide in sediment pore water on-site. This simplified and rapid determination method (ca. 3 min) accurately measured the concentration of hydrogen sulfide without oxidation loss of hydrogen sulfide. XAFS has been used to identify chemical species with minor or no pretreatments, and thus it offers a great advantage over conventional sequential extraction methods by keeping the sulfur species in marine sediments. XAFS can determine redox status and coordination environment for a wide variety of elements, including sulfur, carbon and nitrogen within these sediments. XAFS has been applied to the analysis of the chemical form and oxidation state of sulfur in soil and sediments (Bostick et al., 2005; Jalilehvand, 2006; Burton et al., 2009). Additionally, the collected sediments were immediately stored at 4 °C in vacuum bags to seize/minimize all biological, physical, and chemical activities. The purpose of this study was to reveal the spatial distribution of hydrogen sulfide and sulfur species in coastal marine sediments in Hiroshima Bay, Japan using a combination of the detection tube method and XAFS spectroscopy (Fig. S1).

## 2. Experimental

### 2.1. Study site

Seawater and sediment samples were collected from seven stations in northern Hiroshima Bay, Japan on 2–3 November 2014 (Autumn cruise), 7 February 2015 (Winter cruise), 9 May 2015 (Spring cruise) and 20 August 2015 (Summer cruise) by a training and research vessel, HIKARI, of the National Institute of Technology, Hiroshima College (Fig. 1). The coordinates of the sampling sites are shown in Table S1.

Hiroshima Bay is situated in the Seto Inland Sea, Japan. The enclosed bay is about 30 km from east to west and 50 km from north to south, with a total area of 1043 km<sup>2</sup> and an average depth of 26 m. The bay is significantly affected by intensive oyster culturing (annual production approximately 19,000 tons on an oyster meat basis) and terrigenous loads from the Ota River (catchment area: 1710 km<sup>2</sup>; average river water discharge:  $7.14 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ ; Yamamoto et al., 2002). Station 1 is located near the industrial zone and is affected by domestic and industrial wastewater. Stations 2–4 are situated in the northern part of Hiroshima Bay and are adjacent to a big metropolitan area, Hiroshima city. The terrigenous loads from the Ota River form halocline in the northern part of Hiroshima Bay every summer. Stations 5 and 6 are located in the western part of Hiroshima Bay and were affected by seawater intrusion from the southern part of Hiroshima Bay. Station 7 is located inside the enclosed bay called Etajima Bay where intensive oyster culture is conducted.

### 2.2. Analytical parameters

Vertical profiles of temperature, salinity and dissolved oxygen concentration were measured using a multi probe (AAQ176; JFE Advantec).

Surface sediments were collected at seven stations in the spring, summer and winter using an Ekman-Birge bottom sampler (20 cm × 20 cm; Rigo). In autumn, sediment core samples were collected using an undisturbed core sampler (ø11 cm, 50 cm long; HR type; Rigo) at Sts. 1, 3, 5, 6 and 7. Whereas, at Sts. 2 and 4, the Ekman-Birge bottom sampler was used to collect surface sediments because we could not deploy the undisturbed core sampler due to a strong wind. The collected cores were cut at every 5 cm on board. The surface sediments collected by the Ekman-Birge bottom sampler were taken from the top layer (5 cm). On board, these sediments were immediately transferred into vacuum packs, the air was removed to prevent oxidation and then the packs stored in a refrigerator at 4 °C until they could be transferred to the laboratory. Successively, the sediments were vacuum-dried at 45 °C and ground using an agate-made mortar. The homogenized sediments were stored in vacuum packs to maintain the chemical states of sulfur for XAFS analyses.

The sediment pore water was collected by the rhizon method using a soil moisture sampler that consisted of a syringe and a 50-mm long and ø2.5-mm fiber filter (DIK-305A; Daiki Rika Kogyo). This soil moisture sampler has several advantages when compared with other sampling devices: low mechanical disturbance of the sediment due to the small diameter of 2.5 mm and the absence of direct contact with atmospheric oxygen resulting in minimal loss/oxidation of hydrogen sulfide. The fiber filter was installed in the sediments to suck out a few mL of sediment pore water. The on-site concentration of hydrogen sulfide in the pore water was measured by inserting a detection tube (detection limit: 0.1 mg-SL<sup>-1</sup>) within 3 min (200SB; Komyo Rikagaku Kogyo). The formation of a brown-colored PbS band in the detection tube due to the reaction of hydrogen sulfide and lead is the indicator that hydrogen sulfide is present in the pore water. The length of the brown-colored PbS band in a detection tube is correlated with hydrogen sulfide concentration. The oxidation rate constant of our proposed method ranged from 0.0069–0.0151 min<sup>-1</sup> (Asaoka et al., 2012a). Considering this oxidation rate and the range of observed hydrogen sulfide concentrations, the loss of hydrogen sulfide by oxidation through this procedure was estimated at < 5%.

The oxidation and reduction potential (Eh) and pH of the sediments were measured using Eh and pH electrodes (RM-30P; DKK-TOA, C-62; AS ONE). The total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS) of the sediments were determined by an elemental analyzer (CHNS/O 2400II; Perkin Elmer). The sediment samples were acidified to remove carbonate before TOC, TN, and TS analyses were performed according to the method of Yamamuro and Kayanne, 1995.

For carbon and nitrogen isotope analyses, terrigenous particulate

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