

## Hydrogen sulfide distribution in bottom and pore waters during an anoxic period in Lake Nakaumi, Japan

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**Abstract:** Hydrogen sulfide concentrations in bottom water and surface sediment pore water were measured during an anoxic period (September 2003) in brackish Lake Nakaumi, Japan. Bottom water hydrogen sulfide concentrations were greatest (5–127  $\mu\text{g-SI}^{-1}$ ; except for artificially dredged area) in the southern part of the lake and the Yonago-Bay area, where the hypolimnion is most stagnant, whereas hydrogen sulfide from pore water was detected ( $\sim 1\text{--}37 \text{ mg-SI}^{-1}$ ) in a much wider area. This indicates that surface sediments may maintain anaerobic conditions long after the bottom water return to oxygen rich. Hydrogen sulfide was not detected in bottom and pore waters near the Sakai-Strait and Ohashi River, where seawater and river water flow into the lake. In comparison with two other Japanese brackish lakes (Lake Abashiri and Lake Asokai), Lake Nakaumi has a lower concentration of hydrogen sulfide. Lake Nakaumi is characterized by an unstable hypolimnion, in which anoxic conditions are easily mediated by an oxygen-rich tidal-induced inflow.

**Keywords:** Hydrogen sulfide, anoxic environments, Lake Nakaumi

### Introduction

Bottom water in brackish lakes often becomes anoxic due to the development of a stagnant hypolimnion. Bacterial mats and associated sulfate reduction often occur in anoxic bottom waters and at the redox boundary. These processes are rare in the well-circulated ocean of today, but in the past they did occur during Ocean Anoxic Events (OAE). Therefore, the study of brackish lakes may provide a potential model for geological and geochemical processes in OAE.

Lake Nakaumi, located at the boundary between Shimane and Tottori Prefectures, is an example. It has an area of 86.8 km<sup>2</sup> with average water depth of 5.4 m. Seawater enters through the Sakai-Strait, and river water flows in from the Ohashi River (Fig. 1). The two waters having different densities form a vertical gradient of chemical properties in the lake. For example, the salinity of the upper layer of the lake water is typically about 17

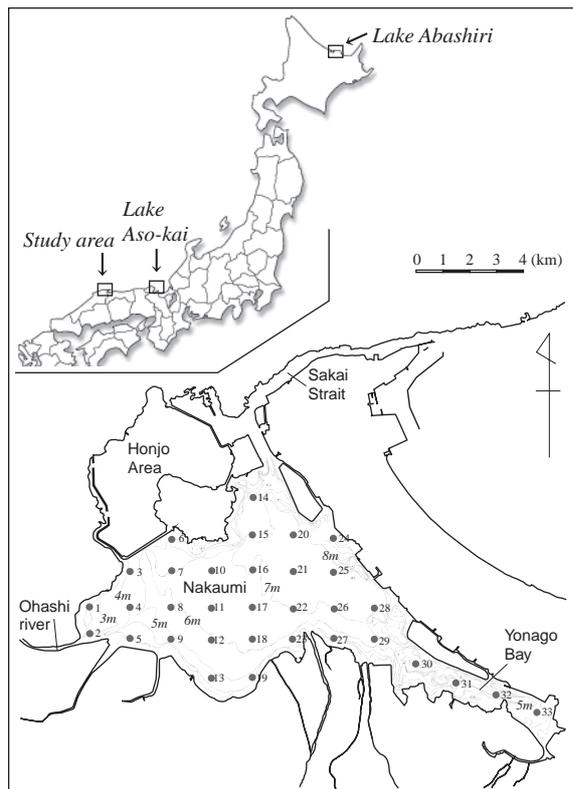
‰ and that of the lower layer is about 27‰ (Date *et al.*, 1989). The vertical gradient in salinity increases during the summer, when the bottom water of the lake develops oxygen-poor or anoxic conditions. This indicates that the lake bottom may be below the redox boundary during summers.

In order to evaluate oxic-anoxic status in coastal lagoon environments (brackish lakes), hydrogen sulfide should be a useful indicator. Okumura *et al.* (1997) reported that the hydrogen sulfide concentration of hypolimnetic water at the deepest site in Lake Nakaumi increased to a maximum of 10.5  $\mu\text{g-SI}^{-1}$  due to the activity of sulfate-reducing bacteria from early summer to autumn. However, no reports have been published describing the spatial distribution of hydrogen sulfide in Lake Nakaumi. Here we present preliminary results on the hydrogen sulfide ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ) concentrations in bottom water and pore water extracted from surface sediments throughout the lake during a time of anoxia

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**Fig. 1.** Sampling locations and bathymetry in Lake Nakaumi.

(September 2003). This research was conducted as a part of the study of brackish waters as a model for past anoxic marine environments in geological history such as Ocean Anoxic Events in Mid-Cretaceous (e.g., Oguri *et al.*, 2002).

## Experimental procedures

### Samples

Samples of lake bottom water and sediment pore water were collected from 33 stations in Lake Nakaumi on 4-7, September 2003 (Fig. 1). At some locations sampling was performed in May, July, August, September, and October 2003 to show seasonal change, as well as vertical distribution in water column.

Hydrogen sulfide concentration was determined using the methylene blue method (Cline, 1969). Because hydrogen sulfide is volatile and easily oxidized, exposure to air and manipulation of the samples must be kept to a minimum. In order to avoid such volatilization of hydrogen sulfide and to simplify the sampling procedure, we modified the method of Cline (1969). Water samples were collected with a Niskin sampler connected to a silicone tube through a petcock. The silicone tube was purged with the water sample for a few seconds. Then a 6-ml plastic syringe, containing 0.4-ml of the appropriate mixed diamine reagent, was connected to the silicone

tube, and a 5-ml water sample was introduced to the syringe. The septum cap was replaced promptly to reduce volatilization of the hydrogen sulfide.

For pore water sampling, surface sediments were collected with Ekman-Birge type bottom sampler. A 10-ml plastic syringe was filled with surface sediment using small spoon. A 0.45- $\mu\text{m}$  filter was connected to the syringe, and the surface sediments in 10-ml syringe were filtered by compressing the 10-ml syringe. The filter was purged with the water sample using pore water pressed through the filter, then a new 1-ml syringe was connected to the filter unit and a 0.5-ml water sample was transferred to 1-ml syringe to which 0.04 ml of the appropriate mixed diamine reagent was added through a three-way cock unit.

At all sampling sites, vertical profiles of temperature, salinity, dissolved oxygen were measured from surface water to just above the surface sediments at 1 m intervals by a calibrated CTD unit (Quanta from Hydrolab Inc.).

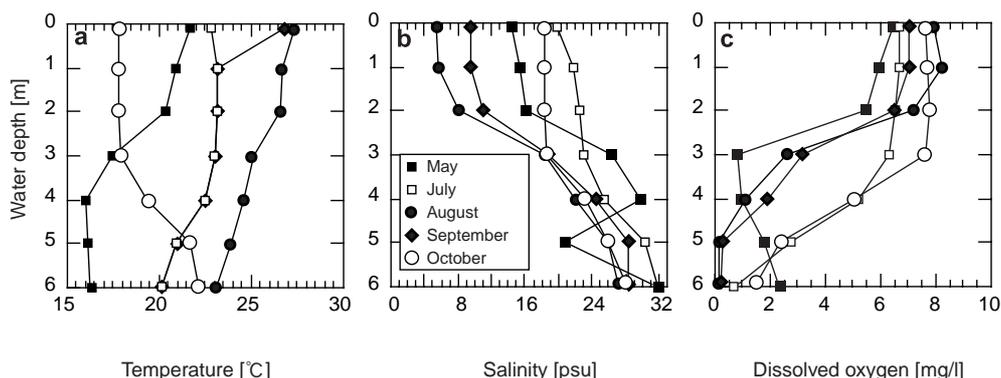
### Quantification

Hydrogen sulfide concentration was determined by a portable absorptiometer (UNIMATER from Tsukuba-Soken Ltd.). All necessary dilutions were made after color development time. The concentration of sulfide in the sample was calculated from the expression,  $C_{\text{SS}} = F(A - A_b)$ , where  $C_{\text{SS}}$  is the concentration of hydrogen sulfide,  $A$  is the absorbance of the sample, and  $A_b$  is the blank absorbance. The factor  $F$  is evaluated by standardization with known concentrations of sulfide (Cline, 1969).

## Results & discussion

### Seasonal variation of vertical profiles

The vertical distribution of water temperature, salinity, and dissolved oxygen in the southern portion of Lake Nakaumi, (Station 18) from May to October 2003 are shown in Fig. 2. Station 18 is one of the sites which has the strongest seasonal change in oxic-anoxic conditions in Lake Nakaumi, as has been shown by the survey of dissolved oxygen in hypolimnetic water done by Shimane Prefectural Inland Fisheries Experimental Station. Bottom water temperatures range from approximately 16°C to 23°C, a slightly smaller amplitude than that of surface water (Fig. 2a). The thermocline gradient is relatively weak and ranges from 3 to 5°C. The salinity of the upper water column fluctuates widely (Fig. 2b), depending primarily on the amount of river water inflow (e.g., Tokuoka *et al.*, 1994), whereas, hypolimnetic water shows relatively little fluctuation. These results indicate that Lake Nakaumi is most strongly stratified in August and September based on the strength of the halocline, which developed in 2003 at a depth of around 3-4 m (Fig. 2b). The upper water column is saturated with



**Fig. 2.** Vertical distributions of (a) water temperature, (b) salinity, and (c) dissolved oxygen in southern Lake Nakaumi (Station 18) from May to October 2003.

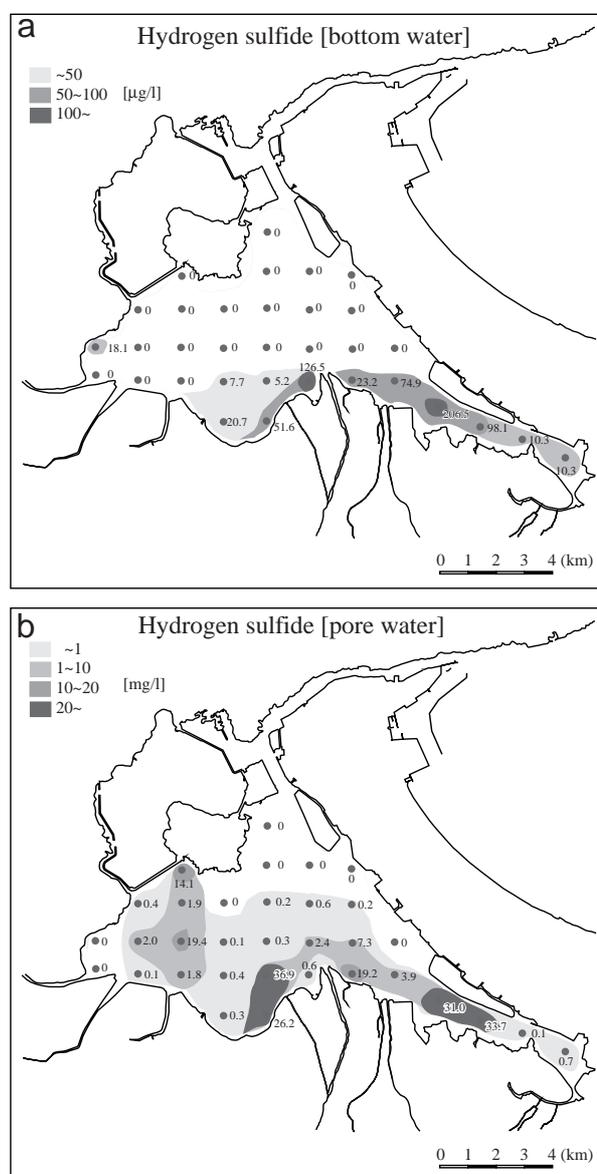
respect to dissolved oxygen (DO) due to gas-exchange with the atmosphere and the high activity of phytoplankton. In contrast, DO decreases at the halocline because the halocline prevents the vertical transport of oxygen and other dissolved components (e.g., Seike *et al.*, 1997). Anoxic water ( $\sim 0.5 \text{ mg-OI}^{-1}$ ) was observed in hypolimnetic water from August to September at a depth below 5 m (Fig. 2 c). The anoxia of September 2003 was therefore used for the study of the distribution of hydrogen sulfide in bottom water and pore water.

#### Distribution of hydrogen sulfide in bottom water and pore water

Hydrogen sulfide was detected in bottom water in the southern part of the lake and the Yonago-Bay area ( $5\text{--}207 \mu\text{g-SI}^{-1}$ ), which are characterized by a relatively stagnant hypolimnion (Fig. 3a). Hydrogen sulfide was not detected in most samples of bottom water in other areas of the lake, although relatively low concentrations ( $\sim 1\text{--}20 \text{ mg-SI}^{-1}$ ) were detected in pore waters (Fig. 3b). In particular, hydrogen sulfide concentrations in pore water in the southern part of the lake and the Yonago-Bay area show relatively high values ( $20\text{--}200 \text{ mg-SI}^{-1}$ ), whereas near the Sakai-Strait and Ohashi River it is undetectable due to the inflow of oxygen-rich seawater and river water.

Hydrogen sulfide concentrations in pore waters were 10 to 200 times larger than those in bottom waters. This suggests that bottom water is more affected by water circulation and diffusion than pore water. In turn, hydrogen sulfide in surface sediments may maintain anaerobic conditions long after the bottom waters return to oxic conditions. The results of Seike *et al.* (1997) support this view. They studied denitrification in Lake Nakaumi and concluded that denitrification can occur when  $\text{NO}_3^-$  and  $\text{NO}_2^-$  is supplied to the reduced substrate even when oxic bottom water was present above the surface sediments.

The distribution of hydrogen sulfide in pore water shows a comparable pattern to that of total organic



**Fig. 3.** Distribution of (a) hydrogen sulfide in bottom water, (b) hydrogen sulfide in surface sediment pore water in Lake Nakaumi, September 2003.

carbon (TOC) of surface sediments shown in Kadokura *et al.* (1998). In 1996, high TOC concentrations (3.5-4.4 %) were recorded in the northwest, central, and southern parts of the lake, and in the Yonago-Bay area. The sediments of the Sakai-Strait and Ohashi river areas (Fig. 1) contained low TOC (~2.5 %). Kadokura *et al.* (1998) suggested that this TOC concentration varied due to redox conditions controlling the decomposition of organic matter. Thus, lower TOC concentrations indicate more oxidized conditions, because DO is the most effective component used for the decomposition of organic matter.

Hydrogen sulfide concentrations in bottom water and pore water have been reported from several other brackish lakes in Japan. Here we compare our results with those from two other well-studied lakes (Lake Asokai and Lake Abashiri) in order to characterize the oxic-anoxic conditions of Lake Nakaumi (Fig. 1). Lake Abashiri, which has the most anoxic bottom water among the three lakes, is characterized by the year-round development of an anoxic hypolimnion (meromictic lake; e.g., Nakao, 1988). Hydrogen sulfide concentrations in the hypolimnion of Lake Abashiri was ~54 mg-SI<sup>-1</sup> and that of pore water in surface sediment was ~66 mg-SI<sup>-1</sup> (unpublished data). These values greatly exceed the values of Lake Nakaumi. The highest hydrogen sulfide concentration measured in Lake Nakaumi was ~127 µg-SI<sup>-1</sup> (except for artificially dredged area) in the summer season (Fig. 3a) and pore water was 6.2 mg-SI<sup>-1</sup> on average (Fig. 3b). In the case of Lake Asokai, which in terms of anoxic conditions is between Lake Abashiri and Lake Nakaumi (Miyaji *et al.*, 1947), hydrogen sulfide concentration of the hypolimnion was ~200 µg-SI<sup>-1</sup> in the summer season and that of the pore water was about 13 mg-SI<sup>-1</sup> on average (Nakanishi *et al.*, 1979). Thus, the concentration of hydrogen sulfide can be used to show that Lake Nakaumi is the least anoxic of the lakes even during its anoxic season. This result can be explained by hydrology of Lake Nakaumi, which, although anoxic conditions develop in the hypolimnion, also has significant inflow from sea and river. This leads to anoxia in hypolimnion that is unstable and easily mediated by tidal-induced inflow containing high dissolved oxygen (e.g., Seike *et al.*, 1997). In areas near the strait and mouth of the river, hydrogen sulfide is only rarely above detectable levels even during the anoxic summer period.

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