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Molecular hydrogen and carbon monoxide in seawater in an area adjacent to Kuroshio and Honshu Island in Japan

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ABSTRACT

Marine H_2 and CO cycles in the sea adjacent to Honshu Island in Japan were investigated using vertical and diurnal seawater sampling. The vertical profiles of the H_2 concentration differed among three stations that were located near the Kuroshio Current, off Suruga Bay, and in the center of Sagami Bay. Surface H_2 enrichment was found near the Kuroshio Current, whereas subsurface H_2 maxima within the pycnocline appeared at the Kuroshio and Suruga Bay stations. Biological N_2 fixation likely accounts for the surface and subsurface H_2 enrichment while the fermentative H_2 production remains as the other possible process. In addition, twenty-four-hour observation at the Sagami Bay station revealed nearly constant H_2 levels through depth and time, whereas a noon-high surface-high pattern was observed in the CO concentrations.

1. Introduction

Molecular hydrogen, H_2, is a reducing molecule and a trace component in oxic modern earth (e.g., Novelli et al., 1999; Ehhalt and Rohrer, 2009). In an oxic marine environment, microbial H_2-oxidizing consumption is thermodynamically favorable and indeed occurs. As a result, H_2 is undersaturated with respect to the air-sea equilibrium in large portions of seawater (e.g., Herr et al., 1981; Herr, 1984). However, local and temporal H_2 supersaturation in seawater has been observed at the sea surface of the lower-latitude ocean and coastal basins (Herr and Barger, 1978; Herr et al., 1984; Lilley et al., 1982; Scranton et al., 1982; Scranton, 1984; Schropp et al., 1987; Setser et al., 1982; Conrad and Seiler, 1988; Moore et al., 2009). From the viewpoint of vertical distribution, the H_2 supersaturation typically appears at the surface (Herr and Barger, 1978; Herr et al., 1984; Conrad and Seiler, 1988) and/or the pycnocline (Herr and Barger, 1978; Schropp et al., 1987) except for deep-sea water near geo-fluid venting fields (e.g., Kawagucci et al., 2010). To date, the noon-high temporal variation (Herr et al., 1984; Conrad and Seiler, 1988) and a positive correlation between the H_2 concentration and chlorophyll a concentration (Setser et al., 1982) have also been noted.

Thus far, three biological and one abiotic H_2 generating processes have been proposed to explain the seawater H_2 supersaturation. Among the four processes, H_2 generation associated with biological N_2 fixation is the most thoroughly documented (Herr et al., 1984; Scranton, 1984; Punshon and Moore, 2008a; Moore et al., 2009). During biological N_2 fixation, which is mediated by the nitrogenase enzyme, H_2 is generated as an obligate byproduct in the following reaction:

$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16P_i\infty. \quad (1)$$

Marine N_2 fixation generally functions by the activity of diazotrophic cyanobacteria in the warm and oligotrophic low-latitude ocean waters (Mahaffey et al., 2005; Shiozaki et al., 2010) where H_2 supersaturation has been found (Herr and Barger, 1978; Herr et al., 1984; Moore et al., 2009; Scranton, 1984; Scranton et al., 1982). In fact, simultaneous measurement of H_2 concentration and biological N_2 fixation rate near the ALOHA station in the central Pacific has revealed a positive linear correlation between them, suggesting the predominance of N_2 fixation in H_2 production in that area (Moore et al., 2009). In addition to the N_2 fixation, biological H_2 production mediated by the hydrogenase enzyme associated with anaerobic fermentation (Schropp et al., 1987) and photosystem (Herr et al., 1984; Min and Sherman, 2010) has been accepted as possible processes that relate to the marine H_2 cycle.

A series of photochemical reactions associated with chromophoric dissolved organic matter (CDOM) are known to generate H_2 (Punshon and Moore, 2008b). It has been proposed that photolysis of marine aldehydes is a source of H_2 (Herr et al., 1984), whereas the aldehydes themselves are products of the photodegradation of marine CDOM (Kieber et al., 1990; Zhou and Mopper, 1997). Observation of lake and estuary water (in which CDOM was highly enriched) and experiments in these waters have revealed surface H_2 supersaturation and a positive correlation between the H_2 production rate and CDOM absorbance (Punshon and Moore, 2008b).

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The CDOM photolysis also generates carbon monoxide (CO), one of the well-studied trace gases in the marine environment (Conrad et al., 1982; Xie et al., 2002; Nakagawa et al., 2004; Ohta, 1997; Zafiriou et al., 2003; Zafiriou et al., 2008). Previous studies have documented the surface-high vertical distribution and noon-high diurnal cycle of marine CO. This typical pattern has been considered to be the result of a combination of photochemical CO production and CO losses by microbial consumption and air–sea gas exchange (e.g., Zafiriou et al., 2003). In addition, marine CO production by phytoplankton (Gros et al., 2009) and through dark abiotic (presumably thermal) reaction (Zhang et al., 2008) have been also pointed out. Because the CDOM photolysis produces both H_2 and CO, simultaneous evaluation of H_2 and CO behaviors in seawater, particularly diurnal variation of them, is expected to provide a useful constraint more accurately to document contribution of the photochemical production for whole H_2 production.

The objective of understanding the marine H_2 cycle includes not only the prediction of its role in the atmospheric H_2 budget with concern for a future hydrogen-economy (Ehhalt and Rohrer, 2009) but also the development of H_2 concentration as a new indicator for the occurrence of biological N_2 fixation (Moore et al., 2009). The current methods for detecting the N_2-fixation activity, acetylene assay and $^{15}N_2$ assay, can provide nitrogen-nutrient flux quantitatively, but essentially require onboard seawater incubation after sampling (Montoya et al., 1996; Konno et al., 2010; Mohr et al., 2010). Onboard H_2 determination has an advantage in immediate detection of the N_2-fixation activity without the need for incubation (Moore et al., 2009) although quantitative conversion from the H_2 production rate to the N_2 fixation rate remains unestablished. Nevertheless, the H_2 indicator, once it is established, does offer potentials in surveying large area of the ocean, detecting local and temporal blooming of diazotrophic cyanobacteria, and guiding the use of the more quantitative incubation-dependent assays. In this study, we established a quick and easy procedure for simultaneous measurement of H_2 and CO in a seawater sample and subsequently observed the temporal and spatial distributions of H_2 and CO in the western North Pacific region adjacent to the Kuroshio Current and Honshu Island in Japan. Possible processes that caused the H_2 enrichment detected at the sea surface and subsurface are discussed.

2. Observations, sampling, and analysis

2.1. Observation and sampling

Seawater samples were collected during the KT-08-14 cruise of the vessel R/V Tansei-maru using a wired Conductivity-Temperature-Depth (CTD)–Carousel-Multiple-Sampling (CMS) system for vertical sampling and a plastic bucket for surface seawater sampling from the gunwale. The wired CTD–CMS system consisted of a CTD profiler (Model 9 Plus, Sea-Bird Electronics), a CMS system (Carousel-32, Sea-Bird Electronics), 12 Niskin-X bottles (12-liter, General Oceanics), a Beckman-type polarographic DO sensor, and an in situ fluorescence sensor (Seapoint Chlorophyll Fluorometer, Seapoint Sensors). Unfortunately, the normal type of Niskin bottles was confirmed to exhibit significant H_2 and CO contamination likely due to the inner tube (data not shown) and was not used in this study.

We conducted vertical hydro-casts from June 27 to July 3 at three stations (Fig. 1 and Table 1), namely, the western North Pacific on the far south of the Honshu Island in Japan (Stn. C: 32°30′N, 138°00′E), off Suruga Bay (Stn. F: 34°30′N 138°30′E), and in the center of Sagami Bay (Stn. G: 35°00′N 139°23′E). The surface seawater at Stn. C was occupied by the Kuroshio water, which is a highly transparent, oligotrophic, warm-water system (e.g., Mizuno and White, 1983). An increase of the filamentous cyanobacteria *Trichodesmium*, which is known as the dominant player in marine biological N_2-fixation activity, and elevation of the N_2-fixation rates were identified in the region from June to August (Shiozaki et al., 2009; Kitajima, 2009). The vertical hydro-casts at Stn. C and Stn. F were conducted before sunset (17:41) and at noon

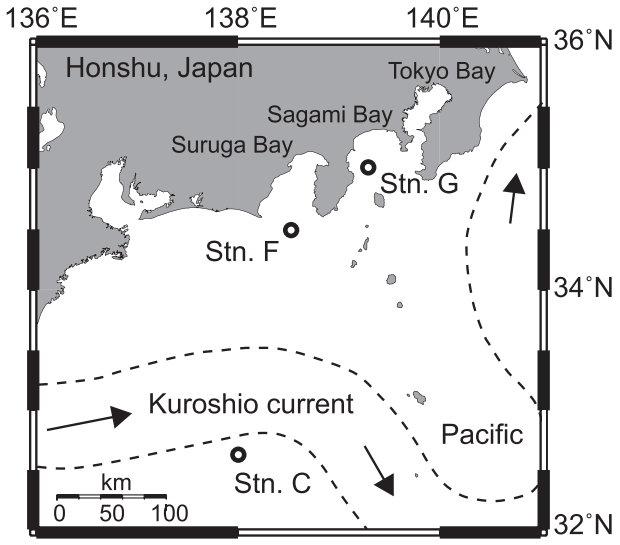

Fig. 1. Map of the study area. Locations of the stations (open circles) in the western North Pacific. The position of the Kuroshio Current during our observation is also presented (data from the Japanese Coast Guard).

(11:22), respectively. At Stn. G, we conducted a series of 24-hour observations via vertical CTD–CMS hydro-casts performed approximately every 6 h (06:00, 13:42, 17:59, 23:58, and 05:59) and surface seawater samplings collected with a bucket at intervals of every 3 h (09:00, 15:00, 21:00, and 03:00 in addition to the five times listed above) from July 2nd to July 3rd. The conditions were mostly sunny during the cruise. The mixed layer depths, defined as the depth at which a change in the surface seawater density (σ_t) of 0.125 occurs (Suga et al., 2004), were 22 m (Stn. C), 6 m (Stn. F), and ~11 m (Stn. G). The vertical DO sensing confirmed oxic seawater throughout the observation, which allowed for aerobic metabolism processes such as H_2 and CO oxidations. Vertical patterns of the in situ fluorescence indicated the maximum intensity at the middle of the pycnocline at all stations that approximately agreed with the phytoplankton chlorophyll a concentrations, determined using subsamples from the Niskin-X bottles by the fluorometric method (Strickland and Parsons, 1972), as modified by Suzuki and Ishimaru (1990), using a fluorometer (Turner Design, Model 10-AU). The sums of the nitrate and nitrite concentrations within the mixed layer were also determined using the subsamples kept frozen prior to the analysis and an onshore nutrient analyzer (AACS-III, BRAN + LUBBE) and ranged between <0.1 μmol-N L^{-1}, 0.1–0.6 μmol-N L^{-1}, and 0.2–.5 μmol-N L^{-1} at stations C, F, and G, respectively (Table 2).

2.2. Analyses

2.2.1. Analytical method

For the H_2 and CO analyses, seawater in the Niskin-X bottles was introduced into the bottom of a 120-mL brown-colored glass vial with no air bubbles via a PTFE tube. The vial was allowed to overflow by >2 volumes before the tube was slowly withdrawn. After the addition of 0.5 mL of $HgCl_2$-saturated solution for poisoning, a PTFE-lined butyl-gum septum was used to cap the vial with an aluminum seal. Duplicate vial subsamples were collected and analyzed from each Niskin-X bottle. From the laboratory experiments, significant H_2 and CO increases were observed when a bare (no-PTFE-lined) butyl-gum septum was used (data not shown). The capped vials were stored in a dark refrigerator (approximately 5 °C) prior to analysis.

The H_2 and CO concentrations were determined at an onboard laboratory within 6 h after subsampling into vials to avoid sample alteration during sample storage (see below). The principle of the analytical method in this study (Fig. 2) was based on a previous work (Xie et al., 2002). To