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Simultaneous Measurement of Hydrogen Peroxide and Fe Species (Fe(II) and $Fe_{(tot)}$) in Okinawa Island Seawater: Impacts of Red Soil Pollution

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The northern part of Okinawa Island suffers from red soil pollution—runoff of red soil into coastal seawater—which damages coastal ecosystems and scenery. To elucidate the impacts of red soil pollution on the oxidizing power of seawater, hydrogen peroxide (HOOH) and iron species including Fe(II) and total iron ($Fe_{(tot)}$, defined as the sum of Fe(II) and Fe(III)) were measured simultaneously in seawater from Taira Bay (red-soil-polluted sea) and Sesoko Island (unpolluted sea), off the northern part of Okinawa Island, Japan. We performed simultaneous measurements of HOOH and Fe(II) because the reaction between HOOH and Fe(II) forms hydroxyl radical (•OH), the most potent environmental oxidant. Gas-phase HOOH concentrations were also measured to better understand the sources of HOOH in seawater. Both HOOH and Fe(II) in seawater showed a clear diurnal variation, i.e. higher in the daytime and lower at night, while $Fe_{(tot)}$ concentrations were relatively constant throughout the sampling period. Fe(II) and $Fe_{(tot)}$ concentrations were approximately 58% and 19% higher in red-soil-polluted seawater than in unpolluted seawater. Gas-phase HOOH and seawater HOOH concentrations were comparable at both sampling sites, ranging from 1.4 to 5.4 ppbv in air and 30 to 160 nM in seawater. Since Fe(II) concentrations were higher in red-soil-polluted seawater while concentrations of HOOH were similar, •OH would form faster in red-soil-polluted seawater than in unpolluted seawater. Since the major scavenger of •OH, Br^-, is expected to have similar concentrations at both sites, red-soil-polluted seawater is expected to have higher steady-state •OH concentrations.

Keywords:
· Fe(II),
· hydrogen peroxide,
· red soil pollution,
· oxidizing power,
· photochemistry,
· hydroxyl radical,
· Okinawa.

1. Introduction

Hydrogen peroxide (HOOH) and hydroxyl radical (•OH) are powerful, naturally occurring oxidants in the environment (Sakugawa *et al.*, 1990; Thompson, 1992; Stumm and Morgan, 1996). HOOH in seawater can be formed from the combination of photochemical reactions of dissolved chemical species (e.g. organic compounds) and gas-to-seawater partitioning of HOOH (Warneck, 1988; Faust *et al.*, 1993; Finlayson-Pitts and Pitts, 2000). Hydroxyl radical can react with many organic compounds at almost diffusion-limited rates, 10^9–10^{10} $M^{-1}sec^{-1}$ (Buxton *et al.*, 1988). The •OH can be formed from the photolysis of various constituents such as nitrate, nitrite, dissolved organic compounds, and $Fe(OH)^{2+}$ in seawater (Zhuang *et al.*, 1992; Faust, 1994; Arakaki and Faust, 1998; Finlayson-Pitts and Pitts, 2000). The •OH can also be formed from the reaction between photo-reduced Fe(II) and HOOH, i.e. the photo-Fenton reaction (Zepp *et al.*, 1992; Arakaki and Faust, 1998).

$$Fe(II) + HOOH \rightarrow \bullet OH + OH^- + Fe(III). \quad (R\text{-}1)$$

In some cases, the photo-Fenton reaction is the dominant pathway of •OH formation in the aqueous phase

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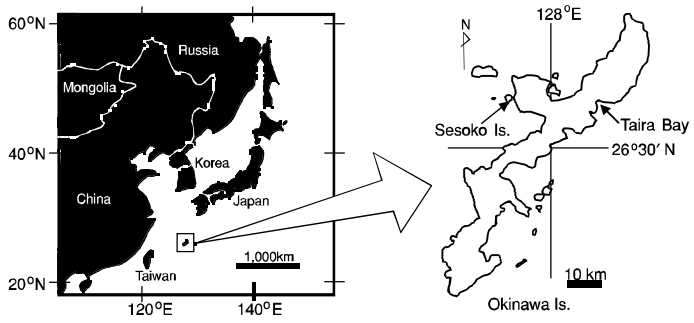


Fig. 1. Sampling locations.

(cloud waters) (Arakaki and Faust, 1998). Thus, it is useful to measure simultaneously the chemical species that react to form the •OH, especially HOOH and Fe(II), to understand the oxidizing power of seawater.

Iron is a ubiquitous element on the surface of the earth. However, because of the low solubility of iron hydroxide (e.g. $Fe(OH)_3$) at the relatively high pH of the ocean (~8), concentrations of dissolved iron are limited in seawater (Faust, 1994). At remote locations, where iron concentrations are low, iron is considered to be the limiting micronutrient for phytoplankton growth (Martin and Fitzwater, 1988).

The northern part of Okinawa Island is covered with red soil, which is dry and of small particle size. Land development, such as pineapple farming and construction of recreational facilities, increases the amount of exposed soil. Every significant rainfall carries red soil easily to the coast, coloring the ocean red. The phenomenon of red soil running off into coastal seawater is locally termed "red soil pollution". Red soil pollution was recognized in the 1980's as responsible for causing significant damage to the growth of corals and fish. Its damage to the ocean, both in terms of its ecosystem and the scenery, is a major concern for Okinawa's tourism industry. Red soil contains 3.5–5% iron, mainly as Fe_2O_3, and is acidic in nature (Vuai *et al.*, 2003a). River waters equilibrated with red soil have been reported to have pH values as low as 4.5 (Vuai *et al.*, 2003a).

We have hypothesized that because of the acidic nature of red soil, seawater contaminated with red soil in the northern part of Okinawa Island will contain increased concentrations of dissolved iron. Since $Fe(OH)^{2+}$ is reported to be a source of OH radicals (Faust and Hoigné, 1990), red soil contaminated seawater could display higher rates of •OH formation, hence stronger oxidizing power, than unpolluted seawater.

Although many studies have been conducted to understand the impacts of red soil pollution on the chemical composition and visibility in seawater (Tokashiki and Nakamura, 1980; Tokashiki, 1993; Vuai *et al.*, 2003a, b), few studies have been conducted to elucidate the effects of red soil on the oxidizing power of seawater. This study was initiated to understand the oxidizing power of red-soil-contaminated seawater by simultaneously measuring concentrations of HOOH, Fe(II), and $Fe_{(tot)}$ (defined here as sum of Fe(II) and Fe(III)). In addition we measured HOOH in the air and seawater in order to better understand the sources of HOOH in seawater.

2. Materials and Methods

2.1 Sampling sites

We chose Taira Bay (128°9′ E, 26°37′ N), Higashi-village, north-eastern part of Okinawa Island as a representative site for red-soil-polluted seawater, and Sesoko Island (127°52′ E, 26°39′ N), on the north-western side of Okinawa Island as a representative site for unpolluted seawater (Fig. 1). Higashi village produces about 1/3 of all pineapples in Okinawa, and is the largest production site in Japan. Sesoko Island is the home of the University of the Ryukyus' Tropical Biosphere Research Center, which is dedicated to studying the diversity of tropical biota including coral reefs and mangroves.

2.2 Seawater sampling, filtration, storage methods, etc.

Seawater and air samples were collected in Taira Bay on November 19–20, 2002 (denoted TB-1), January 9–10, 2003 (denoted TB-2), and in Sesoko Island on January 19–20, 2003 (denoted SI-1) at 2 hour intervals between 06:00–24:00 and at 3 hour intervals between 00:00–06:00. There were no heavy rains (>3 mm in one hour) within 4 days prior to the sampling. Ultraviolet radiation (SD204AB-Cos, Li-COR), air temperature, wind speed and direction were recorded (LI-1000, Li-COR) at 5 minute intervals during the sampling periods. Seawater was collected on the surface using a conventional bucket (polypropylene, 1 L) approximately 3 m away from the piers at both sampling sites. The depth of seawater at both sampling sites was shallow, about 2 m at high-tide and 0.7 m at low-tide. The pH and temperature of the seawater

were measured before filtering the seawater samples. The pH meter (ORION 0290AI) with a ROSS 8102BN pH electrode was calibrated with standard pH solutions (6.863 at 25°C and 4.006 at 25°C) the day before the field measurements.

Immediately after sampling, the seawater samples were filtered through a 0.45 μm PTFE membrane filter (47 mm, Millipore) mounted on polysulfone holders (KP-47S, Advantec). Reddish particles were seen on the PTFE filter when Taira-bay samples were filtered, while almost no particles were seen on the filter after filtering Sesoko samples. Portions of the filtered seawater samples were treated to fix for Fe(II), HOOH, and dissolved organic carbon (DOC) concentrations at the sampling spots. For NO_3^-, NO_2^-, and $Fe_{(tot)}$ measurements, no chemicals were added to the filtered samples. All samples were stored in high density polyethylene bottles (Nalgene) in the dark in a cooler box on ice, transferred, and then stored in the refrigerator (ca. 4°C) at the University of the Ryukyus until chemical analysis. All chemical analyses were completed within 3 days of sample collection.

2.3 Measurement of Fe(II)

Fe(II) and $Fe_{(tot)}$ concentrations in the filtered seawater samples were measured using the HPLC-Ferrozine technique (Yi *et al.*, 1992; Arakaki and Faust, 1998). An 800 μl aliquot of 506 μM Ferrozine was added to 1 ml seawater samples to fix Fe(II) species. The HPLC system used was metal-free and it consisted of a pump (Shimadzu, LC-10Ai), a PEEK injector (Rheodyne 9725i-021), a column (Zorbac Rx-ODS-C18, 4.6 × 250, 5 μm) and a UV-VIS detector (Shimadzu, SPD-10Avp). Retention times and peak heights were used to identify and quantify the Fe(II)-Ferrozine complex. For measurement of $Fe_{(tot)}$, a 100 μl aliquot of hydroxylammonium chloride (0.2%) was first added to 700 μl samples of seawater to reduce all the dissolved Fe(III) species to Fe(II). Next, 200 μl aliquots of 508 μM Ferrozine were added and the Fe(II)-Ferrozine complex was measured by the technique described above. Experimental error for the Fe(II) determination was estimated to be ±3 nM, based on three replicates.

2.4 Measurement of HOOH

Hydrogen peroxide in the air was sampled using a scrubbing coil technique (I.D. 2.0 mm, PFA, 215 cm long) with 1 mM phthalate solution as an absorber (Yamashita *et al.*, 1994). For each sample, 45 L of air was drawn by a pump (SIBATA MP-Σ300) at a rate of 1.5 L min^{-1} for 30 minutes. Hydrogen peroxide and organic peroxides were separated by adding catalase (500 units ml^{-1}) as described in Yamashita *et al.* (1994).

Hydrogen peroxide in the seawater samples and in the phthalate solution was fixed with PEROX regent (Yamashita *et al.*, 1994) at the sampling sites to minimize decomposition of HOOH, and analyzed in the laboratory within 3 days of collection. Experimental error for the HOOH determination was estimated to be ±10 nM, based on replicates.

2.5 Measurement of nitrate, nitrite, DOC

The sum of nitrate (NO_3^-) and nitrite (NO_2^-) concentrations was determined as NO_2^- after reduction of NO_3^- to NO_2^- with the copper-cadmium reduction column technique. The nitrite was then diazotized with sulphanilamide and coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to form an intensely colored azo dye, which was measured colorimetrically (Wood *et al.*, 1967). Absorbance at 540 nm was measured using a HITACHI U-2001 spectrophotometer. Filtered seawater samples (100 ml) were acidified with 1 ml of 0.1 M HCl at the sampling spots for measurement of DOC using a Shimadzu TOC-5000A analyzer.

2.6 Reagents

All reagents were reagent grade or the highest purity available and used as received without further purification. Ferrozine (>98%) was obtained from ACROS ORGANICS. Peroxidase (P 8250, Type II) and catalase (C-40) were purchased from Sigma Chemical Co. All reagent solutions were prepared with Milli-Q water (Millipore, >18 MΩ cm).

3. Results and Discussion

3.1 Chemical composition of red soil contaminated seawater

Table 1 shows the meteorological conditions and chemical composition of seawater at the Taira Bay and Sesoko Island sampling sites. Sampling conditions were mostly clear for TB-1 and SI-1 sampling periods and partly cloudy during the TB-2 sampling period. Wind speeds were less than 3 m sec^{-1} during all sampling periods. Sampling for TB-1 and SI-1 was performed two months apart. The mean air temperature was 21.0°C for TB-1 and 17.9°C for SI-1. The intensity of UV radiation (280–400 nm) between 11:30 to 12:30 was 37.3 W m^{-2} for TB-1 and 33.7 W m^{-2} for SI-1.

Mean values for the sum of NO_3^- and NO_2^- ion concentrations were 0.78 μM, 0.72 μM, and 0.41 μM, for TB-1, TB-2, and SI-1 sampling periods, respectively. These concentrations were comparable to data reported in Crossland (1982) in Sesoko Isalnd, 21 years prior to this study. DOC concentrations were similar at Taira Bay and Sesoko Island (mean = 0.98 ppm for TB-1, 1.21 ppm for TB-2, and 1.04 ppm for SI-1). Observed DOC concentrations were comparable to those found at the Shiraho coral reef site, Okinawa, Japan (Hata *et al.*, 2002), and

Table 1. Meteorological and chemical characteristics of air and seawater in Taira Bay and Sesoko Island.

Time of sampling	Air temp. (°C)	UV ($W\ m^{-2}$)	HOOH (ppbv)	Sea temp. (°C)	HOOH (nM)	Fe(II) (nM)	$Fe_{(tot)}$ (nM)	pH	$[NO_2^-] + [NO_3^-]$ (μM)	DOC (ppm)
November 19–20, 2002 (Taira Bay, TB-1)										
14:00	19.8	35.3	3.7	22.7	100	10	18	8.12	0.50	0.96
16:00	19.4	20.6	3.2	22.7	60	8	20	8.08	0.42	1.10
18:00	19.0	3.2	3.5	22.5	60	7	19	8.07	0.85	1.11
20:00	19.0	0.0	2.8	22.3	60	8	19	8.79	0.67	0.96
22:00	19.4	0.0	3.1	22.2	50	8	19	8.06	0.79	0.88
00:00	19.8	0.0	3.5	21.7	60	8	18	8.02	0.88	0.90
03:00	20.2	0.0	2.4	21.9	50	7	18	8.04	0.64	0.91
06:00	20.2	0.0	3.8	22.5	40	6	21	8.06	0.73	0.93
08:00	21.0	1.5	2.7	22.6	80	8	20	8.08	1.21	0.93
10:00	22.1	12.6	4.1	22.8	70	13	19	8.11	0.93	0.92
12:00	23.2	22.0	4.4	22.9	110	10	19	8.11	0.76	0.95
14:00	23.6	40.9	5.4	23.4	160	10	19	8.10	0.73	1.03
16:00	24.0	26.4	3.3	23.7	120	9	18	8.08	0.88	1.02
18:00	22.9	5.4	3.2	23.6	100	10	19	8.05	0.97	1.10
Mean	21.1	—	3.5	22.7	78	8.6	19.1	8.13	0.80	0.98
S.D.	1.9	—	0.8	0.6	35	1.8	0.9	0.20	0.19	0.08
January 9–10, 2003 (Taira Bay, TB-2)										
14:00	20.8	42.3	4.7	20.4	100	8	18	8.22	0.70	1.42
16:00	15.9	31.7	4.8	20.9	100	7	18	8.25	0.67	1.17
18:00	17.6	8.9	2.4	20.3	100	7	19	8.21	0.58	1.19
20:00	16.9	0.0	2.9	19.9	70	8	19	8.16	0.61	1.15
22:00	15.9	0.0	1.7	19.3	60	10	20	8.16	0.61	1.25
00:00	16.1	0.0	2.2	19.5	60	8	19	8.16	0.64	1.14
03:00	15.8	0.0	2.3	19.4	40	6	19	8.20	0.73	1.17
06:00	15.2	0.0	2.0	18.8	40	8	20	8.16	0.79	1.18
08:00	15.3	0.3	2.8	19.3	60	8	19	8.20	0.92	1.28
10:00	15.3	6.2	2.3	19.5	70	8	20	8.22	0.79	1.24
12:00	16.5	10.5	2.6	19.6	80	7	21	8.21	0.86	1.21
Mean	16.5	—	2.8	19.7	71	7.7	19.3	8.20	0.72	1.22
S.D.	1.6	—	1.0	0.6	22	1.0	0.9	0.03	0.11	0.08
January 19–20, 2003 (Sesoko Island, SI-1)										
14:00	18.8	7.0	3.7	19.9	90	5	15	8.18	0.72	0.95
16:00	18.9	17.4	3.9	20.2	90	6	17	8.22	0.30	0.87
18:00	18.8	5.0	2.5	19.9	70	11	17	8.21	0.11	0.92
20:00	18.1	0.1	2.5	19.5	70	4	16	8.19	N.D.	0.84
22:00	17.8	0.0	2.5	19.1	60	6	17	8.18	N.D.	0.98
00:00	17.8	0.0	2.6	18.8	50	4	18	8.13	1.11	0.89
03:00*	17.4	0.0	2.2	19.2	40	6	17	7.82	16.0	0.95
06:00	17.4	0.0	1.4	17.7	40	4	17	8.01	1.39	1.04
08:00	17.1	0.5	1.5	18.9	30	3	14	8.12	0.11	1.30
10:00	17.4	11.3	1.9	20.0	60	5	14	8.20	N.D.	0.90
12:00	17.9	29.3	3.3	20.1	110	3	16	8.29	0.08	1.35
14:00	17.9	30.3	3.6	20.0	100	6	15	8.29	0.69	1.41
Mean	18.0	—	2.7	19.5	70	5.2	16.0	8.18	0.56	1.04
S.D.	0.6	—	0.9	0.8	25	2.2	1.3	0.08	0.46	0.21

N.D. indicates "Not Detectable".

*Seawater surface was so low because of the low tide (occurred at 02:24) that this seawater sample was collected from a tide pool that retained seawater and the data were omitted from calculation of mean and standard deviation (S.D.).

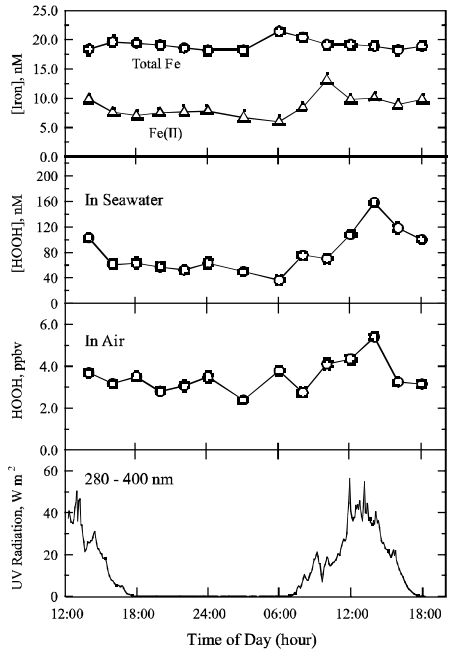


Fig. 2. Diurnal variation of [Fe(II)], [$Fe_{(tot)}$], [HOOH] in seawater, gas-phase HOOH mixing ratio, and UV radiation in Taira Bay, Higashi village, north-eastern side of Okinawa Island during November 19–20, 2002 (TB-1).

were lower than those found in Seto Inland seawater (Fujiwara *et al.*, 1993). Although Taira bay suffers from red soil pollution, DOC concentrations remain relatively low because the red soil does not contain high concentrations of organic matter (Vuai *et al.*, 2003a).

3.2 Fe(II) and total iron concentrations in the seawater

Figure 2 shows the diurnal variation of Fe(II), $Fe_{(tot)}$, seawater HOOH, gas-phase HOOH and UV radiation observed at Taira Bay on November 19–20, 2002 (TB-1). Fe(II) concentrations were highest in the daytime and lowest at night, while $Fe_{(tot)}$ concentrations did not show a clear variation. As Fig. 2 also shows, Fe(II) concentrations reached a maximum at around 10:00, which was a few hours earlier than the maxima for UV radiation and HOOH concentrations in the air and seawater. The reason for this early maximum is probably because the photochemical reduction of Fe(III) species is relatively rapid and reaches steady-state in a short time (Arakakai and Faust, 1998). As HOOH concentrations increase, one would expect photoreduced Fe(II) to be oxidized back to Fe(III) by HOOH via Fenton's reaction. It is noteworthy that nighttime Fe(II) concentrations did not drop to zero, but rather stayed constant (steady state) at 7 nM in coexistence with HOOH. Yi *et al.* (1992) and Kuma *et al.* (1992) suggested that Fe(II) could be formed by microbial reduction.

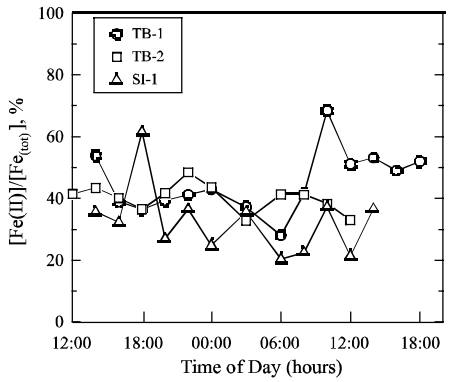


Fig. 3. Diurnal variation of ratio between [Fe(II)] and [$Fe_{(tot)}$] observed in Taira Bay and Sesoko Island during sampling periods.

The mean Fe(II) concentration of samples from Taira bay (red-soil-polluted) was 8.2 nM, which was 58% higher than the mean Fe(II) concentration of 5.2 nM for samples from Sesoko Island (un-polluted) (Table 1). The mean concentration of total Fe ($Fe_{(tot)}$) for samples from Taira Bay was 19 nM, 19% higher than the mean value of 16 nM for seawater samples from Sesoko Island. Kuma *et al.* (1992) found $Fe_{(tot)}$ concentrations between 20–40 nM in Funka Bay, Japan and Hirata *et al.* (1999) found $Fe_{(tot)}$ concentrations of 67.7 nM in coastal seawater samples. Total Fe concentrations found in Taira Bay are not particularly high for the near shore seawater samples. Rue and Bruland (1995) and van den Berg (1995) found that more than 99% of dissolved iron was bound to organic compounds in seawater. Low DOC concentrations in Taira Bay and Sesoko Island seawater probably limit the dissolution of iron from red soil, accounting for lower $Fe_{(tot)}$ concentrations.

Figure 3 shows the diurnal variation of the ratio between Fe(II) and $Fe_{(tot)}$ for the three sampling periods. On average, 43% and 33% of iron exists as Fe(II) at Taira Bay and Sesoko Island, which is similar to the values reported by Yi *et al.* (1992). For seawater samples collected at TB-1, Fe(II) concentrations reached approximately 70% of the total iron concentrations during the daytime, which is comparable to the values reported for cloud waters (Arakaki and Faust, 1998), indicating photochemical reduction of Fe(III) species.

3.3 HOOH concentrations in the gas phase and in the seawater

Figure 2 also shows the diurnal variation of gas-phase and seawater HOOH concentrations observed at Taira Bay during the TB-1 sampling period. HOOH concentrations in both the gas phase and seawater reached a maximum at around 14:00 (solar noon was 12:15 on November 20,

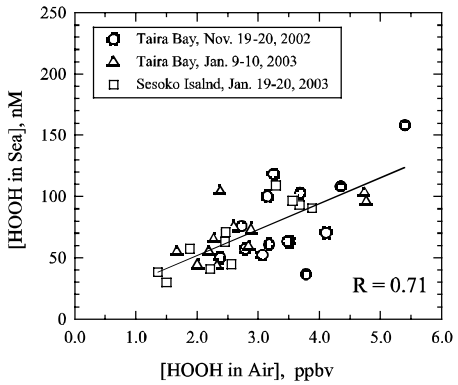


Fig. 4. Correlation between [HOOH] in seawater and the gas-phase HOOH mixing ratio in Taira Bay and Sesoko Island during the three sampling periods. The solid line is a least-squared regression line for all data points.

2002). In Taira Bay and Sesoko Island, HOOH concentrations ranged from 1.4 to 5.4 ppbv in the gas phase and 30–160 nM in the seawater and did not show significant differences between the two sampling sites. Gas-phase HOOH concentrations found in Okinawa were compatible with aircraft measurements over remote regions of the Pacific and South Atlantic Ocean reported by O'Sullivan *et al.* (1999) and ground-based measurements at a remote coastal site in Ireland (Morgan and Jackson, 2002). Seawater HOOH concentrations were also compatible with values obtained for near-surface seawater in the South and central Atlantic Ocean (Yuan and Shiller, 2001).

There are two possible sources of HOOH in seawater during unclouded daylight; one is in situ photochemical formation and the other is air-to-seawater partitioning. Photochemical reactions of dissolved organic compounds can form HOOH in the aqueous phase (Cooper and Zika, 1983; Faust *et al.*, 1993; Fujiwara *et al.*, 1993; Anastasio *et al.*, 1994). Based on TB-1 data, the HOOH production rate between 10:00 and 14:00 was 22 nM hour^{-1}. Yocis *et al.* (2000) reported mean HOOH photoproduction rates of 4.5 nM hour^{-1} in Antarctic waters, and 9 nM hour^{-1} in the Mediterranean Sea (Johnson *et al.*, 1989). Because DOC concentrations in the studied seawater were relatively low (ca. 1 ppm) at both sites, photochemical formation of HOOH alone may not account for the calculated production rate.

Another source of HOOH in seawater is gas-to-seawater partitioning of HOOH. Because the Henry's law constant for HOOH is $K_H = 1 \times 10^5$ M atm^{-1} (Finlayson-Pitts and Pitts, 2000), seawater-to-air transfer is unlikely to occur. If 1 ppbv of gas-phase HOOH is at equilibrium with seawater, then the seawater HOOH concentration is calculated to be 100,000 nM (100 μM), much higher than the observed seawater HOOH concentrations (on average 73 nM). Thus, equilibrium is not reached between air and seawater, and it is expected that gas-phase HOOH is transferred to seawater.

Figure 4 shows the correlation between gas-phase HOOH and seawater HOOH concentrations (R = 0.71). Since both gas-phase HOOH and seawater HOOH can be formed by photochemical reactions, it is not possible to differentiate between the two sources of HOOH in seawater based on the correlation. Gas-to-seawater transfer of HOOH is also a complex process, affected by wind speed and boundary conditions between air and seawater (e.g. stagnant 2-film model, Schwarzenbach *et al.*, 1993). Further study is needed to distinguish the two sources of HOOH and to better understand the contribution of each source to seawater HOOH concentrations on sunny days.

3.4 Impacts of red soil pollution on oxidizing power of seawater

This study found that Fe(II) and $Fe_{(tot)}$ concentrations in Taira Bay (red-soil-polluted sea) were on average 58% and 19% higher than those in Sesoko Island (unpolluted sea). Gas-phase HOOH concentrations and seawater HOOH were comparable at both sampling sites. The sum of nitrate and nitrite and DOC concentrations were also comparable at both sites. Based on these observations, it is inferred that the •OH formation rate (R_{OH}) from the Fenton reaction could be up to 58% greater in red-soil-polluted seawater.

In seawater, it is reported that •OH is mainly scavenged by high concentrations of Br^- ion (Mopper and Zhuo, 1990). Steady-state •OH concentrations ($[•OH]_{ss}$) can be calculated by the following equation (Arakaki and Faust, 1998):

$$[•OH]_{ss} = R_{OH}/(k_{OH+Br} \times [Br^-])$$

where (R_{OH}) is the •OH formation rate, k_{OH+Br} is a bimolecular rate constant for the reaction between •OH and Br^- (1.1×10^{10} M^{-1}sec^{-1}, Buxton *et al.*, 1988) and [Br^-] is the concentration of Br^- in seawater (ca. 0.8 mM). Because concentrations of Br^- in red-soil-polluted seawater and unpolluted seawater would not be very different, steady-state concentrations of •OH would be higher in the red-soil-polluted seawater.

Since red-soil pollution is mainly caused by human activities (i.e. land development for farming and construction), it is expected that concentrations of agricultural chemicals for farming and wastes from human activities are also increased near the red-soil-polluted coastal area. With the higher steady-state concentrations of •OH, these pollutants could be oxidized faster in red-soil-polluted seawater, hence the lifetimes of these pollutants may be shorter than in unpolluted seawater.

4. Summary

We have conducted simultaneous measurement of hydrogen peroxide (HOOH) and iron species (Fe(II) and $Fe_{(tot)}$) in red-soil-polluted and unpolluted seawater off the northern parts of Okinawa Island to better understand the effects of red soil on the oxidizing power of seawater. Both HOOH and Fe(II) showed a clear diurnal variation, i.e. higher during the daytime and lower at night. Fe(II) concentrations were approximately 58% higher in the red-soil-polluted seawater samples than in unpolluted seawater. No clear effects of red soil pollution on HOOH concentrations were observed in the seawater.

Red soil pollution has been recognized as a serious environmental problem. We demonstrate in this study that red-soil-polluted seawater contains higher concentrations of Fe(II). At similar concentrations of HOOH, higher Fe(II) concentrations will increase the formation rate of OH radical via Fenton's reaction and therefore increase the oxidizing power of red-soil-polluted seawater.

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