

---

# A Subject of the Chlorine Management at a Thermal Power Plant on the Northwest Pacific Ocean in Japan

Toshio Iibuchi, Seiji Kobayashi, Sigenori Nanjou, Kanako Satou, Takeya Hara, and Michiyasu Kiyono

---

## Abstract

The concentration of chlorine residue was monitored near the outlet of a large thermal power plant in Japan. The plant is required by the local government to ensure that the concentration of chlorine residue remains below 0.05 mg/L at the outlet. Background levels of chlorine residue were relatively high, though lower than 0.05 mg/L. There was a significant positive correlation between the concentrations of phytoplankton and the background concentrations of chlorine residue. About 0.3 mmol/L of H<sub>2</sub>O<sub>2</sub> was required to produce a color reaction equivalent to the background signal in the *N-N*-diethyl-*p*-phenylenediamine assay for chlorine residue. However, reported concentrations of H<sub>2</sub>O<sub>2</sub> in the Sargasso Sea are only 0.0002 mmol/L. H<sub>2</sub>O<sub>2</sub>, which is produced by phytoplankton, oxidizes Br<sup>-</sup> and I<sup>-</sup> to produce HBrO and HIO. We hypothesize that these oxidants react with reagents in the *N-N*-diethyl-*p*-phenylenediamine assay and are naturally produced chlorine residuals.

---

T. Iibuchi (✉) • M. Kiyono  
Marine Ecology Research Institute,  
Towa-Edogawabashi Bldg., 347 Yamabuki-cho,  
Shinjyuku-ku, Tokyo 162-0801, Japan  
e-mail: [iibuchi@kaiseiken.or.jp](mailto:iibuchi@kaiseiken.or.jp)

S. Kobayashi  
JAPAN NUS Co., Ltd., Nishi-Shinjuku Kimuraya  
Bldg., 7-5-25 Nishi-Shinjuku, Shinjuku-ku, Tokyo  
160-0023, Japan

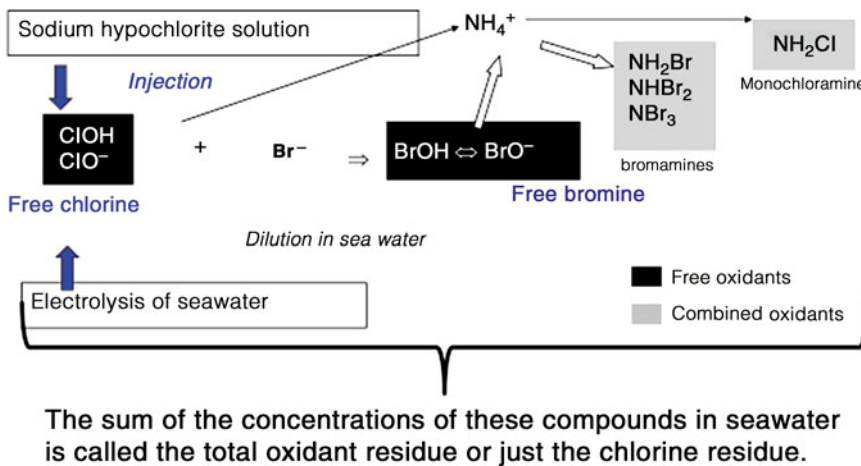
S. Nanjou • K. Satou  
Soma Kyodo Power Co., Ltd., Shinchi Power Station,  
1-1 Imagami, Komagamine, Shinchi-Town, Soma  
County, Fukushima 979-2611, Japan

T. Hara  
Marine Ecology Research Institute, Central  
Laboratory, Onjukumachi, Isumigun, Chiba  
299-5105, Japan

---

## 1 Introduction

Power plants that use seawater for their cooling water usually suffer from biofouling. Chlorine is often used to lessen biofouling and the associated damage to the plant. When chlorine is added to seawater, it oxidizes bromide ions, the product being hypobromous acid (HBrO). Hypobromous acid reacts with ammonia, and a variety of oxidants (mainly bromamines) are subsequently generated. The sum of concentrations of these substances is referred to as the total oxidant residue (or just “chlorine residue”) in seawater (Fig. 1). In many cases, Japanese power plants are required by local governments to keep the



**Fig. 1** In seawater, the total oxidant residue (chlorine residue) consists mainly of free bromine and bromamines (Redrawn from Khalanski 2002)

concentration of the chlorine residue under the limit of quantitation (LOQ) at the outlet. According to the Japanese Industrial Standards (JIS), the LOQs of the chlorine residue are 0.05 and 0.01 mg/L as Cl for the *N-N*-diethyl-*p*-phenylenediamine (DPD) and orthotolidine methods of analysis, respectively (Japanese Standards Association 2002).

## 2 Methods

### 2.1 Sampling of Seawater and Phytoplankton

Seawater samples from a depth of 0.5 m at stations 1–8 and from a depth of 6 m at stations 1–6 were obtained with a reciprocal pump in the vicinity of a thermal power plant on the coastline of Japan facing the Western North Pacific Ocean (Fig. 2). The dates of sampling were 30 September, 24 October, 2 December, and 20 December 2011 at stations 1–8 and 27 January, 21 February, and 15 March 2012 at stations 1–6. For about 1 year, including this period, the injection of chlorine into the intake of the power plant was stopped.

Phytoplankton samples were obtained from a depth of 0.5 m at stations 1, 2, and 4 at the same time as the seawater sampling. The phytoplankton in 10 L of seawater were filtered

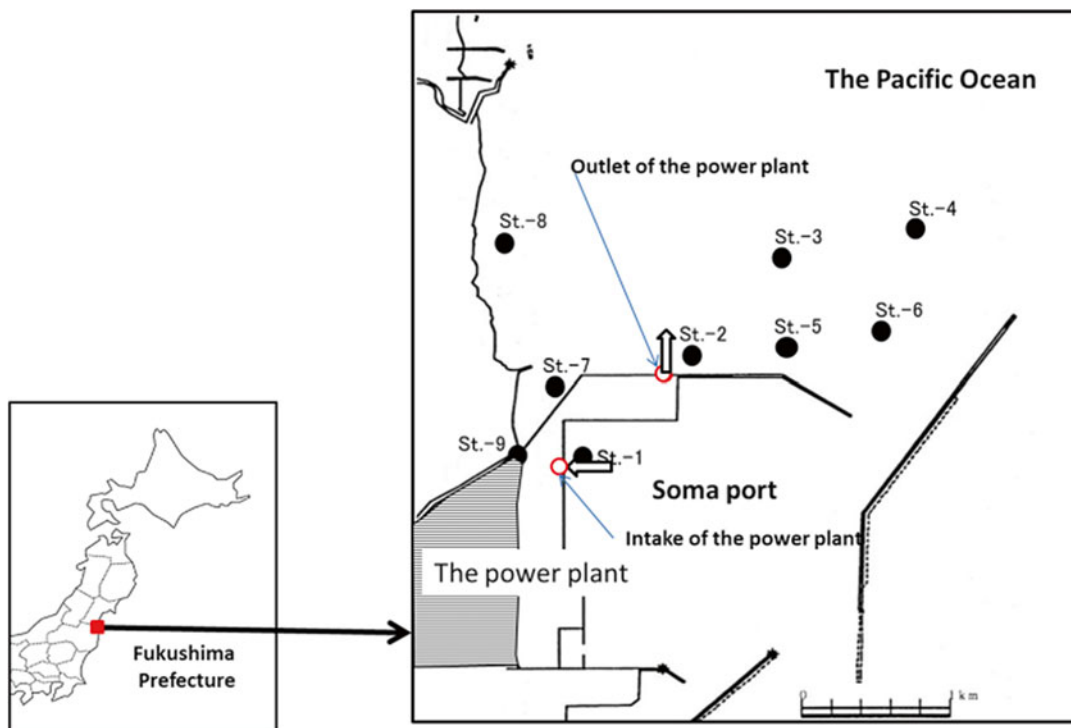
through a 20- $\mu$ m mesh-size net on board the boat, concentrated into 200 mL seawater, and preserved with 30 mL of 33 % formaldehyde solution. Samples were stored in the dark under cool conditions. Professionals at the Plantbio Co., Ltd., Odawara, Japan, classified and counted the phytoplankton cells.

### 2.2 Measurement of Chlorine Residue

We used both the DPD and orthotolidine colorimetric methods to measure the chlorine residue in water samples on board the boat immediately after obtaining the samples. The detailed analytical methodology of the DPD method is described in Standard Methods (Rice et al. 2012), and that of the orthotolidine method is described in JIS Handbook Environmental Technology (Japanese Standards Association 2002).

### 2.3 Temperature Effects on Measurements of Chlorine Residuals

Sensitivity tests for the two colorimetric methods of chlorine quantitation were conducted on 28 June, 4 August, and 17 November 2012 and 2 February 2013. We used each colorimetric



**Fig. 2** Map of the sampling locations in northern Fukushima, Japan

method to measure the chlorine residue in the same sample solution at different temperatures. The concentration of the chlorine residue in each sample was predetermined using an iodometric titration, which is more accurate than either colorimetric method. The sample solutions were prepared by adding sodium hypochlorite to seawater and then leaving the solutions to stand for more than 60 min to allow the concentration of chlorine residue to stabilize. The solutions were held at a temperature of 10, 15, 20, 25, or 30 °C during the measurements. The temperature of 30 °C was used only in the summer. The analytical methodology of the iodometric titration is described in Standard Methods (Rice et al. 2012).

## 2.4 Interference by $H_2O_2$ in the Measurement of Chlorine Residue

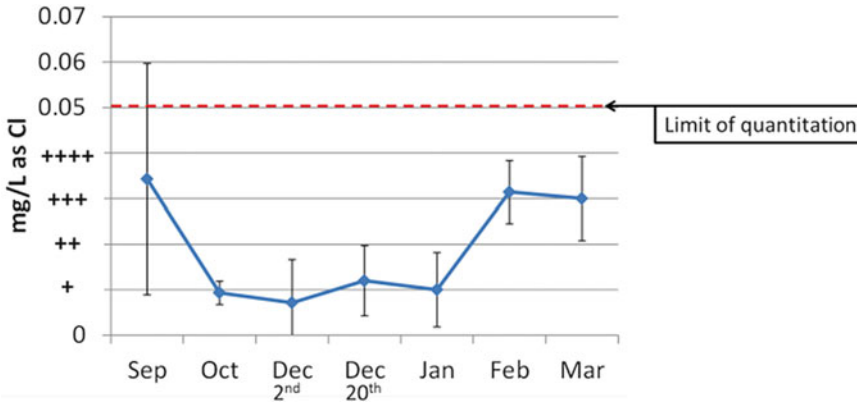
To study the reactions between  $H_2O_2$  and the reagents in the DPD and orthotolidine assays, we

measured the color changes that occurred in a NaCl solution and in filtered seawater in which  $H_2O_2$  was dissolved. The NaCl solution was prepared by dissolving 35 g of NaCl in 1 L of distilled water. In the case of the DPD method, 0.03 mL of 35 %  $H_2O_2$  (11 mmol) was added to 1 L of NaCl solution and to 1 L of seawater. In the case of the orthotolidine method, 0.3 mL of 35 %  $H_2O_2$  (105 mmol) was similarly added to 1 L of NaCl solution and to 1 L of seawater.

## 3 Results and Discussion

### 3.1 Field Survey of Chlorine Residue

The results of the field survey of chlorine residue based on the DPD method are shown in Fig. 3. The DPD reagent develops a weak red color even at the limit of quantitation. We ranked the extent of the redness as +, ++, +++, and +++, corresponding to solutions that were made by diluting



**Fig. 3** Concentrations of chlorine residue measured by the DPD method during the period when chlorination was stopped. Concentrations below the limit of quantitation

were characterized by the symbols +, ++, +++, and +++++, according to the extent of *red color* development in the DPD assay

the standard color solution (0.05 mg/L as Cl) to 0.01, 0.02, 0.03, and 0.04 mg/L as Cl, respectively. The results show a significant amount of background chlorine residue, even though the injection of chlorine at the power plant was stopped during the period of sampling. In the results obtained with the orthotolidine method, the background concentrations were lower (data not shown).

### 3.2 Temperature Effects on Measurements of Chlorine Residue DPD Method

The chlorine residue concentrations determined by the iodometric titration method (abscissa) are compared with those obtained by the DPD method (ordinate) in Fig. 4. An analysis of covariance indicated that there was no statistically significant temperature effect on the slopes of the linear relationships between the results obtained by the two methods. The elevations of the regression lines, however, were significantly different; the y-intercepts in spring and summer were higher than in autumn and winter (Fig. 5;  $p < 0.01$ ).

#### 3.2.1 Orthotolidine Method

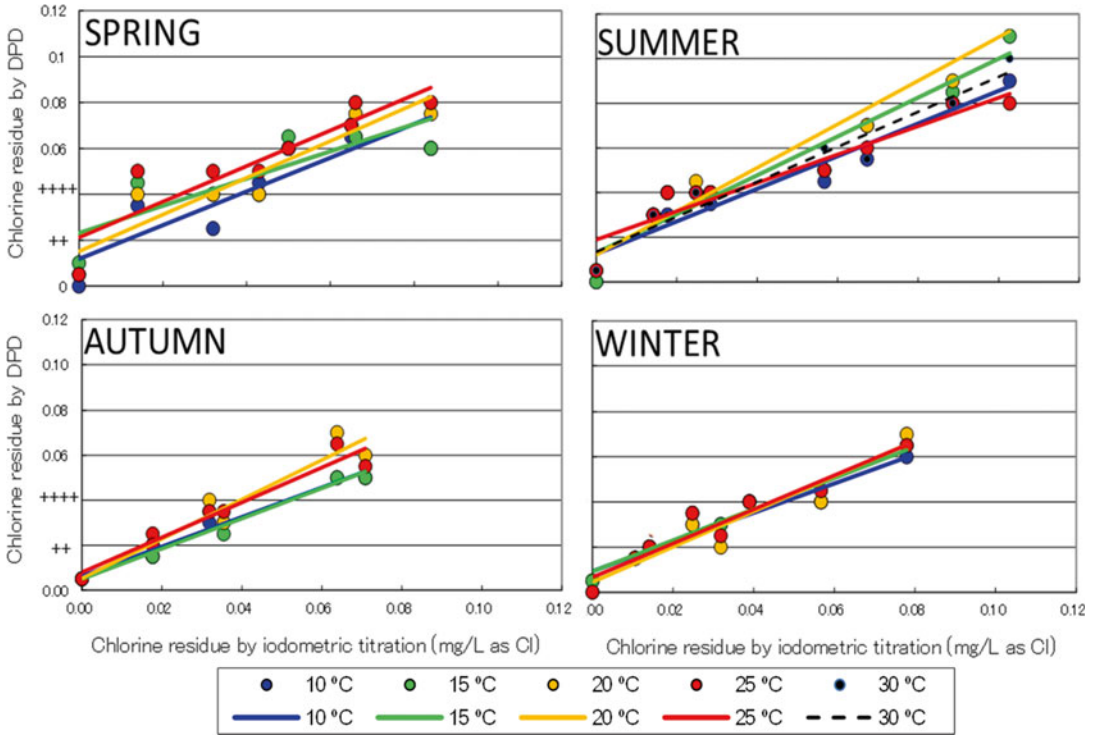
In the case of the orthotolidine method, the slopes of the lines were small (about 0.2–0.7) and differed among temperatures and between seasons (Fig. 6;  $p < 0.01$ ). The implication is that the chlorine residue estimated with the orthotolidine method was affected by the temperature of the water sample. The orthotolidine method tends to give a lower value than the iodometric titration and DPD methods.

### 3.3 Concentrations of Phytoplankton

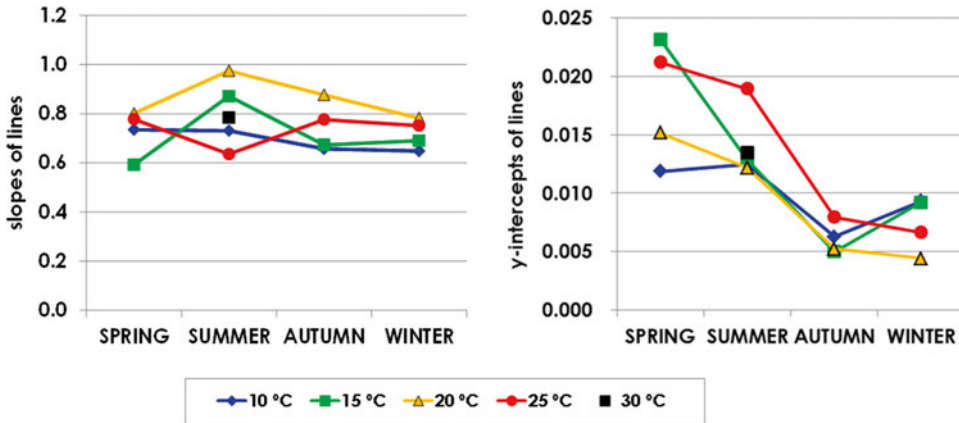
The phytoplankton concentration data are shown in Fig. 7 (left). The concentrations at each site were similar and decreased from autumn to winter.

#### 3.4 Interference by H<sub>2</sub>O<sub>2</sub> in the Measurement of Chlorine Residue

The results of the assays for chlorine residue with H<sub>2</sub>O<sub>2</sub> dissolved in NaCl solution and filtered seawater are shown in Fig. 8. In the DPD assay, with 11 mg/L of H<sub>2</sub>O<sub>2</sub> dissolved in the water, the arti-



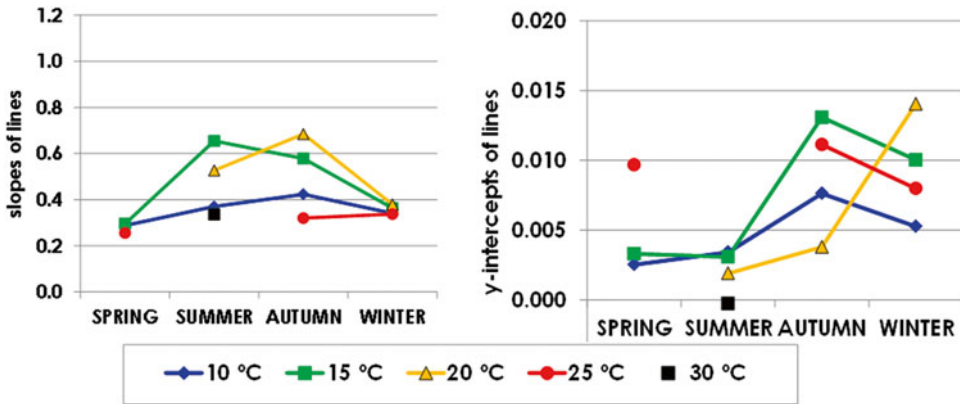
**Fig. 4** Comparison of the chlorine residue estimated with the iodometric titration method (abscissa) and with the DPD method (ordinate)



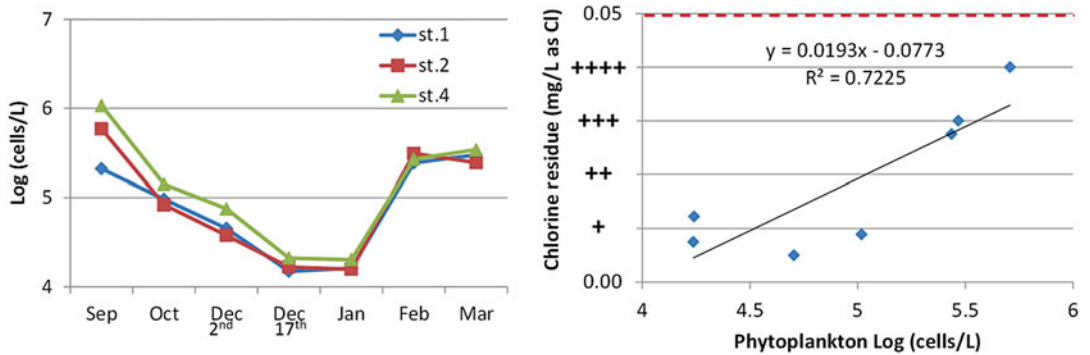
**Fig. 5** The slopes (left) and the y-intercepts (right) of the lines in Fig. 4

factual chlorine residue concentrations were 0.09 mg/L as Cl and ++ (0.02 mg/L as Cl equivalent) in the NaCl solution and filtered seawater,

respectively. In the orthotolidine assay, with 105 mg/L of H<sub>2</sub>O<sub>2</sub> dissolved in the water, the artificial chlorine residue concentrations were only

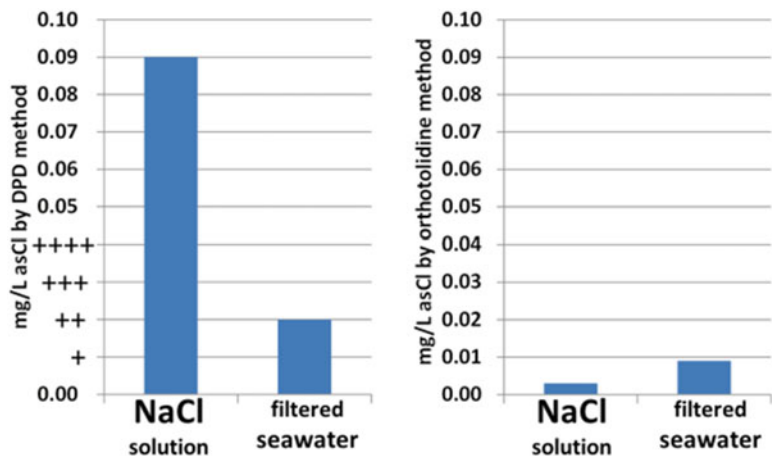


**Fig.6** The slopes (*left*) and the y-intercepts (*right*) of lines relating chlorine residue estimated with the iodometric titration and orthotolidine methods

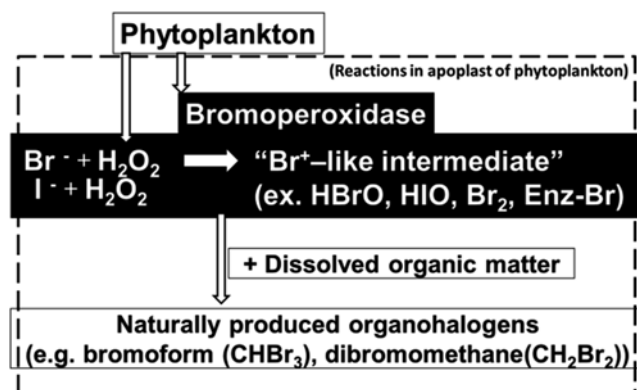


**Fig. 7** Concentrations of phytoplankton (*left*) and the relationship between the concentrations of phytoplankton and chlorine residue (Data from Fig. 3) estimated by the DPD method (*right*)

**Fig. 8** Interference by  $H_2O_2$  in the measurement of chlorine residue. The  $H_2O_2$  concentration in the water was 11 mg/L in the DPD assay (*left*) and 105 mg/L in the orthotolidine assay (*right*)



**Fig. 9** A scheme for the production of chlorine residue (HBrO) and organo halogens by phytoplankton (Redrawn and modified from Tschirret-Guth and Butler 1994)



about 0.003 mg/L as Cl and 0.009 mg/L as Cl equivalent in the NaCl solution and filtered seawater, respectively.

#### 4 Discussion

Comparison of the DPD and iodometric titration (Figs. 4 and 5) results indicates the existence of an unknown material that causes the background signal to be larger with the DPD method than with the iodometric titration method in spring and summer. On the basis of our experience, we hypothesized that the unknown material responsible for the chlorine residue blank was a by-product of phytoplankton photosynthesis. We believe that the positive correlation between the concentrations of phytoplankton and chlorine residue estimated with the DPD method (Fig. 7, right) supports our hypothesis. There is also a possibility that some abiotic mechanism is responsible for the blank; for example, strong solar radiation may produce oxidants in the atmosphere or in the sea (Plane et al. 1997). At first, we assumed that  $\text{H}_2\text{O}_2$  was the naturally produced unknown material that was interacting with the DPD reagents because  $\text{H}_2\text{O}_2$  has been reported to be one of the substances that interfere with the measurement of chlorine residue by the DPD method (Japanese Standards Association 2013).

According to the literature,  $\text{H}_2\text{O}_2$  is produced in phytoplankton cells (Palenic et al. 1987; Twiner and Trick 2000). But to produce a red color in the DPD assay equivalent to a chlorine residue concentration of ++ (0.02 mg/L as Cl equivalent), 11 mg/L (0.3 mmol/L) of  $\text{H}_2\text{O}_2$  was required (Fig. 8), which is about 1,500 times the reported concentration in the Sargasso Sea [at most 0.0002 mmol/L; Miller and Kester (1994)]. Recently, several species of diatoms have been reported to catalyze the oxidation of  $\text{Br}^-$  and  $\text{I}^-$  by  $\text{H}_2\text{O}_2$ , the products being HBrO and HIO (Hill and Manley 2009). Such reactions are catalyzed by bromoperoxidase and iodoperoxidase on the surface of the cell (in the apoplast; Fig. 9; Tschirret-Guth and Butler 1994; Lin and Manley 2012). These mechanisms probably account for the low concentration of  $\text{H}_2\text{O}_2$  in the sea, because oxidation of  $\text{Br}^-$  and  $\text{I}^-$  (and the simultaneous reduction of  $\text{H}_2\text{O}_2$ ) may occur continuously in the apoplast of the cell, where the concentration of  $\text{H}_2\text{O}_2$  is as high as it is in higher plants and macroalgal species (Küpper et al. 2002). As mentioned above, the regulations relating to chlorination by power plants in Japan are very strict. If the results of this study are found to be generally applicable in the future, the strict regulation of chlorination at Japanese power plants should be reconsidered. The background concentration must be added to the threshold value (LOQ, i.e., 0.05 mg/L as Cl for the DPD method). We believe that identification

of the substances responsible for the background concentration should be a priority.

**Acknowledgment** This research program was carried out under a contract with the Soma Kyodo Power Company, Ltd., Japan.

## References

- Hill VL, Manley SL (2009) Release of reactive bromine and iodine from diatoms and its possible role in halogen transfer in polar and tropical oceans. *Limnol Oceanogr* 54(3):812–822
- Japanese Standards Association (2002) (eds) JIS Handbook Environmental Technology
- Japanese Standards Association (2013) (eds) JIS Handbook of Environmental Technology II – water chemistry analysis (in Japanese)
- Khalanski M (2002) Organic products generated by the chlorination of cooling water at marine power stations. *Journées d'Etudes du Cebedeau, Tribune de l'Eau* No. 619-620-621, France, 24–39
- Küpper FC, Muller DG, Peters AF, Kloareg B, Potin P (2002) Oligoalginat recognition and oxidative burst play a key role in natural and induced resistance of sporophytes of Laminariales. *J Chem Ecol* 28(10):2057–2081
- Lin CY, Manley SL (2012) Bromoform production from seawater treated with bromoperoxidase. *Limnol Oceanogr* 57(6):1857–1866
- Miller WL, Kester DR (1994) Peroxide variations in the Sargasso Sea. *Mar Chem* 48:17–29
- Palenic B, Zafriou OC, Morel FMM (1987) Hydrogen peroxide production by a marine phytoplankter. *Limnol Oceanogr* 32(6):1365–1369
- Plane JM, Blough NV, Ehrhardt MG, Water K, Zepp RG, Zika RG (1997) Photochemistry in the sea surface micro layer. In: Liss P, Duce R (eds) *The sea surface and global change*. Cambridge University Press, New York, pp 71–92, 536 pp
- Rice EW, Baird RB, Eaton AD, Clesceri LS (eds) (2012) *Standard methods for examination of water and wastewater 2012*. American Public Health Association, Washington, DC, 1496 pp
- Tschirret-Guth RA, Butler A (1994) Evidence for organic substrate binding to vanadium bromoperoxidase. *J Am Chem Soc* 116:411–412
- Twiner MJ, Trick CG (2000) Possible physiological mechanisms for production of hydrogen peroxide by the ichthyotoxic flagellate *Heterosigma akashiwo*. *J Plankton Res* 22(10):1961–1975