

## Where's the cadmium in biogenic particulate matter?

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**Abstract** A preliminary study on the cadmium (Cd) distribution in biogenic particulate matter was carried out in the subtropical sea near Ishigaki Island. Almost all of the biogenic Cd was determined to be associated with the organic materials, and the possibility of the estimation of the Cd adsorbed onto the surface of organic materials and associated with metalloproteins was suggested; however further methodological examination such as checking the dissolution of the calcium carbonate ( $\text{CaCO}_3$ ) phases (hard protective shell) during the chemical leaching treatment of acid hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) might be necessary.

**Key Words:** cadmium, biogenic particulate matter, chemical leaching treatment, subtropical sea

Many reports on the good correlation of cadmium (Cd) behavior with marine biogeochemical processes have been published in the last two decades (e.g., de Baar *et al.*, 1994), suggesting an important role of marine biota such as phytoplankton for the Cd carrier regulating the distribution in the ocean; however, which part in the planktonic organisms (such as calcium carbonate ( $\text{CaCO}_3$ ) phases (hard protective shell) and organic materials) is an efficient carrier has not been clearly elucidated. The objective of this short paper is to report a preliminary study on the distribution of Cd in biologically produced particulate matter, which is considered to be the first step for the topic noted above.

Surface water samples were taken at five stations on the 123° E line (St. 1: 24° 00' N; St. 2: 23° 30' N; St. 3: 23° 00' N; St. 4: 22° 30' N; St. 5: 22° 00' N) in the subtropical sea near Ishigaki Island using an acid-cleaned plastic bucket aboard the R/V Yoko-Maru of the Seikai National Fisheries Research Institute (SNFRI) on March 9 and 10, 2003 (YK02-14) (Fig. 1). The samples for particulate Cd were collected by filtration (8.75 L) through a

0.6- $\mu\text{m}$  Nuclepore filter (Corning) on board, and the filters were frozen immediately at  $-40^\circ\text{C}$ . In this study, biogenic particulate Cd was defined as two fractions for the convenience's sake, i.e.; acetic acid

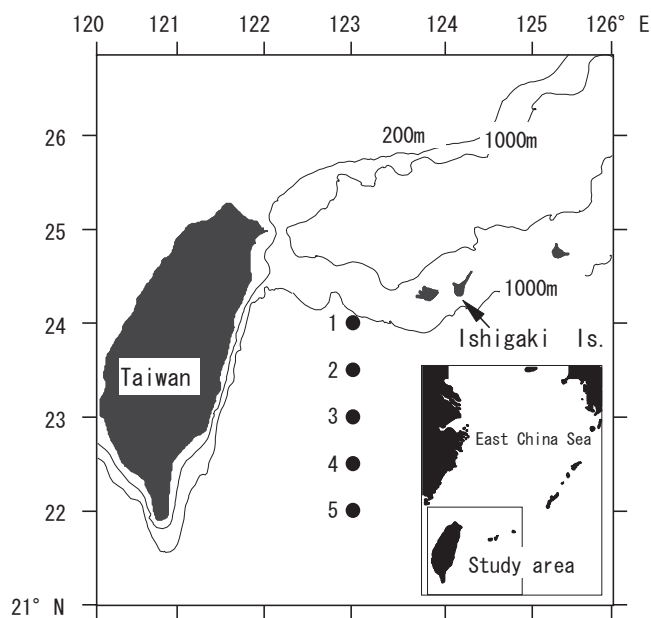
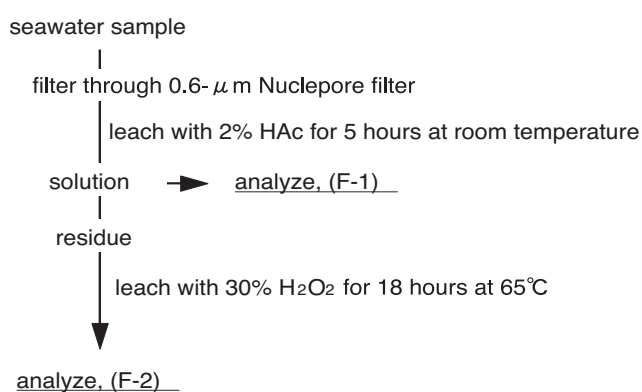


Fig. 1. : Sampling sites in this study

(HAc) leachable and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) soluble fractions. In general, these fractions are considered to be adsorbed cations, carbonate phases, and associated with metalloproteins (HAc) (Collier and Edmond, 1984; Löscher *et al.*, 1998), and the Cd in organic materials ( $\text{H}_2\text{O}_2$ ), respectively (Kitano *et al.*, 1980; Noriki *et al.*, 1997). Usually, in the chemical leaching experiment using HAc and  $\text{H}_2\text{O}_2$ , HAc leaching has been conducted prior to  $\text{H}_2\text{O}_2$  treatment. However, this procedure can't discriminate the Cd in the HAc leachable organic materials from the Cd associated with  $\text{CaCO}_3$  (adsorbed and incorporated). So, in this study, determination of Cd was examined by two procedures as follows (Fig. 2):

#### Experiment-1



#### Experiment-2

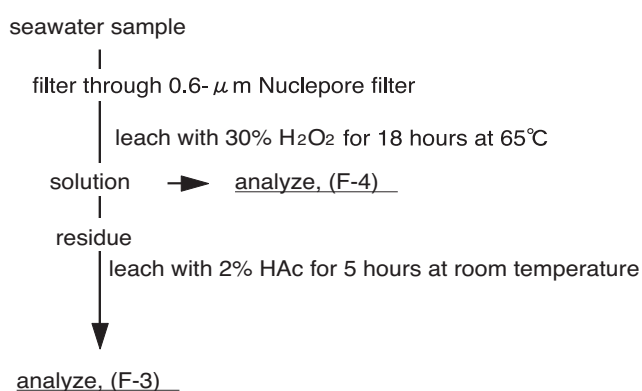


Fig. 2. : Flow diagram of selective chemical leaching techniques

1) Experiment-1 (Ex.-1): Particulate Cd on a 0.6- $\mu\text{m}$  Nuclepore filter was put into 2 mL of 2% HAc solution for 5 hours at room temperature, and the solution was filtered through a 0.4- $\mu\text{m}$

Nuclepore filter (F-1). The residue on the filter was transferred into a Teflon vessel; 2 mL of 30%  $\text{H}_2\text{O}_2$  solution was added and kept at 65°C for 18 hours (F-2). This procedure was carried out for samples from all stations.

2) Experiment-2 (Ex.-2): The order of chemical leaching in Ex.-1 was changed; namely 30%  $\text{H}_2\text{O}_2$  treatment (F-4) was carried out prior to 2% HAc leaching (F-3). This procedure was carried out for only one sample from St. 5. The determinable Cd in each fraction is shown in Table 1, and combining these two procedures made it possible to determine the Cd in the HAc leachable organic phases, namely adsorbed onto the surface of organic materials and associated with metalloproteins (difference between (F-1) and (F-3), and (F-4) and (F-2)). All the procedures for Cd analysis were conducted in a laminar flow bench, and the Cd in these fractions was determined by atomic absorption spectrophotometry (using a Hitachi Z-8270 flameless atomic absorption spectrophotometer (AAS)). A standard addition method was adopted for the determination to correct for matrix interference, and the standard solution was prepared from a commercially available standard solution (1000 ppm, Wako Chemicals). The grade of used chemical reagents, HAc and  $\text{H}_2\text{O}_2$  were the S. S. G and S (Wako Chemicals), respectively. Blank values (Cd) of the procedure were 0.009 pM and 0.012 pM for HAc and  $\text{H}_2\text{O}_2$  treatment, respectively.

Seawater analysis data were listed in Table 2. Salinity (using a Tsurumi Seiki Degi-Auto 3-G salinometer) and temperature (thermometer on board) were in the range 34.87-34.97 and 22.8-25.2°C, respectively. Phosphate ( $\text{PO}_4$ ) and dissolved Cd (by colorimetry and AAS described in Abe (2002)) were almost depleted, and in regard of these parameters, it is considered to be no great differences in the oceanographic conditions among the sampling sites in this study. Although a microscopic observation of the collected particulate matter was not carried out in this study, relative abundance of the surface phytoplankton near this study sites (22°30' N; 124°40' E) have been reported as 54.6, 38.5, and 6.9% for dinoflagellates, haptophyceae, and diatom, respectively (SNFRI,

**Table 1.** Determinable Cd in each fraction

Ex.-1 : HAc (F-1)	①	②	③	④	
Ex.-1 : H <sub>2</sub> O <sub>2</sub> (F-2)					⑤
Ex.-2 : HAc (F-3)	①	②			
Ex.-2 : H <sub>2</sub> O <sub>2</sub> (F-4)			③	④	⑤

\*① : adsorbed onto the surface of CaCO<sub>3</sub> phases

\*② : incorporated into the CaCO<sub>3</sub> phases

\*③ : adsorbed onto the surface of organic materials

\*④ : associated with metalloprotein

\*⑤ : in the rest of the organic materials

2000). Table 3 shows the concentrations of Cd and the percentages to the determined total biogenic Cd (in the parentheses) in each fraction ((F-1), (F-2), (F-3), and (F-4)). From Ex.-1, the concentrations of particulate Cd in the (F-1) and (F-2) fractions varied from 0.40 to 0.59 pM and from 0.072 to 0.13 pM, respectively. From Ex.-2, (F-3) and (F-4) fractions were 0.015 pM and 0.49 pM, respectively, which suggested that almost all (97%) of Cd was in the organic fraction. Furthermore, by subtracting (F-3) from (F-1, average) and (F-2, average) from (F-4), much similar Cd concentrations were calculated as 0.46 and 0.39 pM, respectively, showing the possibility of the estimation of the Cd adsorbed

onto the surface of organic materials and associated with metalloproteins using the combination of two methods described in this study although only one result for (F-3) and (F-4) fractions has been obtained from St.5. However, the possibility of part of the CaCO<sub>3</sub> dissolution into the acid H<sub>2</sub>O<sub>2</sub> solution (pH; around 4.0) under heating treatment at 65°C for 18 hours could not be eliminated (which could lead to the overestimation of the determined (F-4) fraction), and checking this dissolution is considered to be a problem to be solved in future. Thus, further methodological examination such as the electron microscopic observation of the CaCO<sub>3</sub> dissolution during the chemical leaching treatment

**Table 2.** Seawater analysis results

	Temp. (°C)	Salinity	PO <sub>4</sub> (μM)	dissolved Cd (nM)
St. 1 (0m)	24.0	34.97	nd	nd
St. 2 (0m)	22.8	34.95	nd	nd
St. 3 (0m)	22.9	34.96	nd	0.007
St. 4 (0m)	25.2	34.87	0.08	nd
St. 5 (0m)	24.3	34.97	nd	0.008

\* Less than 0.05 μM of PO<sub>4</sub>, and 0.007 nM of Cd (2.5 times of the deviation of the blank) are shown as "nd".

**Table 3.** Concentration of Cd in each fraction. Percentages are shown in parentheses.

	(F-1) (pM, (%))	(F-2) (pM, (%))	(F-3) (pM, (%))	(F-4) (pM, (%))
St. 1 (0m)	0.40 (75)	0.13 (25)		
St. 2 (0m)	0.59 (84)	0.11 (16)		
St. 3 (0m)	0.43 (80)	0.11 (20)		
St. 4 (0m)	0.43 (86)	0.072 (14)		
St. 5 (0m)	0.52 (85)	0.089 (15)	0.015 (3)	0.49 (97)
average	0.47 (82)	0.10 (18)		

of H<sub>2</sub>O<sub>2</sub> might be necessary.

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