

生物起源粒子中のどこにカドミウムは存在するか?

メタデータ	言語: English
	出版者: 水産総合研究センター
	公開日: 2024-10-02
	キーワード (Ja):
	キーワード (En): cadmium; biogenic particulate matter;
	chemical leaching treatment; subtropical sea
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URL	https://fra.repo.nii.ac.jp/records/2010814
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短 報

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 (CaCO₃) phases (hard protective shell) during the chemical leaching treatment of acid hydrogen peroxide (H_2O_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 roll 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 (CaCO₃) 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- μ m Nuclepore filter(Corning)on board, and the filters were frozen immediately at -40°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

2004年7月16日受理 (Received on July 16, 2004)

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(HAc) leachable and hydrogen peroxide (H_2O_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 (H_2O_2) , respectively (Kitano *et al.*, 1980; Noriki *et al.*, 1997). Usually, in the chemical leaching experiment using HAc and H_2O_2 , HAc leaching has been conducted prior to H_2O_2 treatment. However, this procedure can't discriminate the Cd in the HAc leachable organic materials from the Cd associated with CaCO₃ (adsorbed and incorporated). So, in this study, determination of Cd was examined by two procedures as follows (Fig. 2):

Experiment-1

seawater sample

filter through 0.6- μ m Nuclepore filter

leach with 2% HAc for 5 hours at room temperature

solution → <u>analyze, (F-1)</u> residue leach with 30% H₂O₂ for 18 hours at 65°C

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analyze, (F-2)
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Experiment-2

seawater sample

filter through 0.6- μ m Nuclepore filter

leach with 30% H2O2 for 18 hours at 65°C

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solution - <u>analyze, (F-4)</u>
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residue

leach with 2% HAc for 5 hours at room temperature

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analyze, (F-3)
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Fig. 2. : Flow diagram of selective chemical leaching techniques

1) Experiment-1 (Ex.-1): Particulate Cd on a 0.6- μ 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- μ 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% 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% H₂O₂ 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 regents, HAc and H_2O_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 H₂O₂ treatment, respectively.

Seawater analysis data were listed in Table 2. Salinity (using a Tsurumi Seiki Degi-Auto 3 -G salininometer) and temperature (thermometer on board) were in the range 34.87-34.97 and 22.8-25.2°C, respectively. Phosphate (PO₄) 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 ou in each fraction						
Ex1 : HAc	(F-1)	1	(2)	3	(4)	
$Ex1:H_2O_2$	(F-2)					(5)
Ex2 : HAc	(F-3)	(1)	(2)			
$Ex2:H_2O_2$	(F-4)			3	(4)	(5)

Table 1. Determinable Cd in each fraction

*(1): absorbed onto the surface of CaCO₃ phases

*⁽²⁾: incorporated into the CaCO₃ phases

*(3) : absorbed onto the surface of organic materials

 $*(\underline{4})$: assosiated 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

Table	2.	Seawater	analysis	results
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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 CaCO₃ dissolution into the acid H₂O₂ 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 CaCO₃ dissolution during the chemical leaching treatment

	Temp.	Salinity	PO_4	dissolved Cd
	(°C)		(μM)	(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 μ M of PO₄, 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)	(F-2)	(F-3)	(F-4)
	(pM, (%))	(pM, (%))	(pM, (%))	(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 H₂O₂ might be necessary.

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生物起源粒子中のどこにカドミウムは存在するか?

阿部 和雄(西海区水産研究所石垣支所) 沖縄県石垣島近海の亜熱帯海域表層における生物起 源粒子(炭酸カルシウムの殻及び有機物)中のカドミ ウムを調べた。その結果,生物起源カドミウムの多く が有機物区分に存在していた。また,過酸化水素水に よる加熱抽出時における炭酸カルシウム殻の溶解の可 能性等が考えられ,今後の検討課題として残された。 No.13, 11-14 (2004)