

# The accumulation rate and benthic fluxes for selenium in the marginal seas

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## Abstract

This paper describes the concentrations of selenite, selenate and organic selenide in pore water, and selenium in sediment cores in the marginal seas. The selenium accumulation rates for the Sulu Sea and the South China Sea were 1.16 and 0.21 mg cm<sup>-2</sup>yr<sup>-1</sup>. The upward diffusive fluxes of dissolved selenium were estimated by using Fick's first law. The calculated fluxes of dissolved selenium as selenate in the Sulu and South China Seas were estimated to be 0.17 and 0.88 μg cm<sup>-2</sup>yr<sup>-1</sup>, respectively.

*Keywords:* selenium, accumulation rate, benthic flux, marginal sea

## 1 Introduction

Selenium is one of trace essential element. Selenium has three chemical forms such as selenite, selenate and organic selenide in sea water. Some investigators reported the vertical profiles of three selenium species in open seas (Measures and Burton, 1980; Measures et al., 1983; Cutter and Cutter, 1995, 1998, 2001, Hattori et al., 2001a, Nakaguchi et al., 2004, Sherrard et al., 2004).

There are few reports for the selenium speciation in pore water and sediment (Takayanagi and Belzile, 1988, Weres et al., 1989, Fio and Fujii, 1990, Zhang and Moore, 1996, Belzile et al., 2000, Velinsky and Cutter, 1991). Then the behavior of selenium (diagenesis) is still unknown. In this paper, selenium accumulation rate was calculated by using analytical values of selenium

concentration in marginal sea sediment samples collected from the Celebes, Sulu and South China Seas. In addition, the benthic fluxes for selenium were estimated.

## 2. Material and methods

### 2.1 Sampling

All sediment samples were collected on during the KH-02-4 cruise of R/V Hakuho-Mar. Sampling locations are shown in Fig. 1. Sediment cores were collected at the Sulu Sea station (St.13) and the South China Sea station (St.18) during the KH-02-4 cruise. Multiple corers were used for sediment sampling. The core was cut immediately after recovery at 0.5-cm intervals in the top 2 cm and 1.0-cm intervals in the rest of the core. A part of each sample sectioned from one core was provided for pore water analyses, and the rest was sealed in a vial for the measurement of water content. Pore water samples were squeezed from the sectioned sediment samples under air-tight conditions in a thermostated refrigerator at in-situ temperature filtration through a 0.45  $\mu\text{m}$  membrane filter, using a hydraulic pressure type squeezer (Kato et al., 1996). Sediment excluding and pore water extracting were performed within 48 hr in the walk-in refrigerator laboratory at  $4 \pm 2$  °C. The concentrations of nitrate, nitrite, phosphate and silicic acid in pore water were immediately determined with the Autoanalyzer (BRAN+LUEBBE Co., Ltd). The sediment and pore water samples for selenium speciation were placed in separate polyethylene tubes, and then frozen immediately after squeezing.

### 2.2 Chemical Analysis

The pore water samples used for

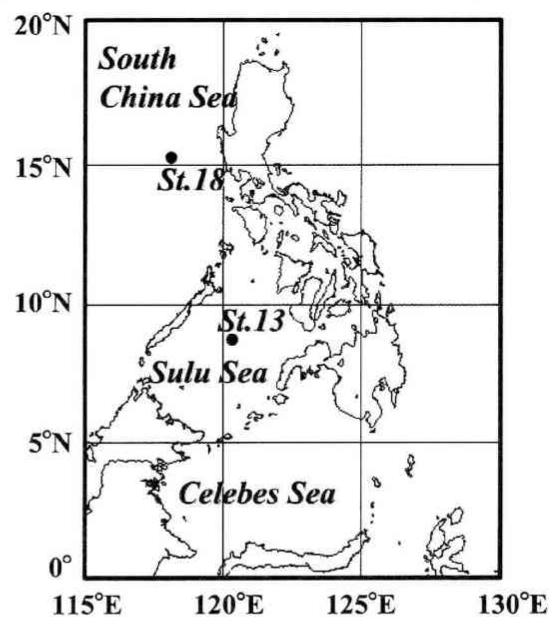


Fig.1 Sampling locations

speciation were diluted appropriately after thawing. The analytical procedures for selenium speciation in the pore water have been described elsewhere (Hattori et al., 2001b). Selenium was determined by HPLC with a fluorescence detector. For HPLC, a JASCO (Japan Spectroscopic Co. Ltd.) intelligent HPLC system 800 series equipped with a Hitachi L-7480 fluorescence detector (150W xenon-lamp) and Hitachi D-2500 Chromato-Integrator were used. The sample injector was a Rheodyne 7125 stainless sample injector with a 100  $\mu\text{l}$ -sample loop. The separation column was a Cosmosil 5 SL-II Packed Column (4.6 i.d. x 150mm, Nacalai Tesque Co. Ltd.) filled with silica gel.

The preparation method for determination of total selenium in the sediment core samples: After squeezing to remove pore water, sediment core samples were placed in polyethylene tubes and the contents were dried by a freeze dry method. Next the sediment core samples were decomposed by a wet ashing method with nitric acid + perchloric acid +

hydrofluoric acid (Kubota et al., 1995). After decomposition, all selenium species in the sample were reduced to selenite by hydrochloric acid, and then selenite was determined as described above.

The concentration of selenium determined in the open ocean sea water CRM NASS-5 (National Research Council of Canada) corresponded to the certified and information value. The concentrations of selenium determined in the estuarine sediment SRM 1646a (National Institute of Standards & Technology) corresponded to the certified and information values.

### 3. Results and discussion

#### 3.1 The concentrations of selenium in pore water and sediment.

The concentration of selenium in pore water and sediment samples are shown in Table 1.

Table 1 The concentrations of selenium in pore water and sediment

Sampling station	Depth (cm)	Pore water (nmol/l)				Sediment (mg/kg)
		Total Se	Selenite	Selenate	Organic Se	Total Se
Sulu Sea St.13	0-1	47.8	12.4	10.1	25.3	0.41
	1-2	28.0	6.6	1.8	19.6	0.24
	2-3	19.1	2.8	1.5	14.8	0.28
	3-4	10.5	4.5	0.0	9.9	0.06
	4-5	17.2	3.4	0.3	13.4	0.17
	5-6	16.5	1.8	3.8	11.0	0.08
	6-7	21.7	—	—	17.4	0.21
	8-9	22.3	3.5	—	—	0.28
	10-11	35.0	6.4	0.0	30.0	0.22
	13-14	9.9	5.4	1.6	2.9	0.32
	16-17	26.8	5.4	0.0	21.6	1.39
South China Sea St.18	0-0.5	179.1	54.6	26.6	97.9	0.16
	0.5-1	122.0	13.7	29.5	78.9	0.15
	1-1.5	111.1	0.0	35.6	75.5	0.24
	1.5-2	72.1	10.4	18.8	43.0	—
	2-3	79.9	0.0	23.8	56.1	0.00
	3-4	34.0	0.0	12.6	21.4	0.24
	4-5	34.2	1.1	12.9	20.2	0.01
	5-6	42.0	0.3	13.1	28.6	0.19
	6-7	43.9	0.0	28.3	15.6	0.31
	7-8	28.6	0.0	14.3	14.3	0.21
	8-9	24.8	0.3	9.1	15.5	0.47
	9-10	19.6	0.0	7.8	11.7	0.82
	10-11	22.4	0.7	4.3	17.4	0.70
	11-12	19.6	0.8	3.6	15.2	0.50
	12-13	21.6	0.6	9.5	11.5	0.54
	13-14	23.1	0.6	6.8	15.7	0.39
	14-15	21.3	0.9	6.9	13.5	0.03
	15-16	20.4	0.6	8.9	10.8	0.12
	16-17	20.3	0.5	6.4	13.4	0.44
	17-18	19.5	0.6	6.6	12.3	0.24
18-19	12.9	0.0	3.7	9.3	0.22	
19-20	9.6	0.0	4.8	4.8	0.23	
20-21	13.6	0.0	6.1	7.4	0.23	
21-22	17.0	0.0	5.1	11.9	0.31	
22-23	9.2	0.1	4.9	4.2	0.15	
23-24	8.9	0.0	3.8	5.0	0.33	

#### 3.2 The selenium accumulation rate for the Sulu and South China Sea.

The particulate organic selenide in deep-sea is derived primary from biological production in surface waters. The high surface productivity leads to high particulate organic selenide enrichment of underlying sediments. Although surface production is very important, other factors such as sediment accumulation rates and sediment mixing intensities also play an important role. Kuehl et al. determined the accumulation rates by the sea-bed profiles of <sup>14</sup>C. The accumulation rates for the Sulu Sea and the South China Sea were 2.57-5.78g cm<sup>-2</sup> kyr<sup>-1</sup> and 1.34-1.74 g cm<sup>-2</sup> kyr<sup>-1</sup>, respectively (Kuehl et al., 1993). The concentrations of selenium in the surface sediment in the Sulu Sea station St.13 and the South China Sea station St.18 were 0.41 and 0.16 mg kg<sup>-1</sup>, respectively. The bulk accumulation rates were 2.82 g cm<sup>-2</sup> kyr<sup>-1</sup> in the Sulu Sea at BC#9(most near St. 13) and 1.34 g cm<sup>-2</sup> kyr<sup>-1</sup> in the South China Sea at BC#2(most near St.18), respectively. The calculated selenium accumulation rates for the Sulu Sea and the South China Sea were 1.16 and 0.21 mg cm<sup>-2</sup> yr<sup>-1</sup>, respectively. The selenium accumulation rate for the Sulu Sea is 5.5 times higher than the South China Sea. This may be due to the difference between the primary production of two sea area. The chlorophyll level in the Sulu Sea is significantly higher than the level in the South China Sea (Jones, 2002). The average weight percentages of carbonate in the Sulu Sea sediment (ca.60%) was higher than that in the South China Sea sediment (ca. 40%), and also the organic carbon accumulation rate for the Sulu Sea (10.2 mgC cm<sup>-2</sup> yr<sup>-1</sup>) was higher than that for the South China Sea (5.05 mgC cm<sup>-2</sup> yr<sup>-1</sup>) (Kuehl et al., 1993). These data suggested

that the amount of biogenic particulate matter in the Sulu Sea is greater than that in the South China Sea. The higher accumulation rate for the Sulu Sea depends on the higher primary production.

Kuehl et al. determined the mixing coefficients by  $^{210}\text{Pb}$  profiles. The corrected mixing coefficient for the South China Sea ( $0.503 \text{ cm}^2 \text{ yr}^{-1}$ , BC#2) was higher than that for the Sulu Sea ( $0.099 \text{ cm}^2 \text{ yr}^{-1}$ , BC#9). The dissolved oxygen at bottom in the South China Sea ( $2.64 \text{ ml l}^{-1}$ , Gamo, 1997) was higher than that in the Sulu Sea ( $1.28 \text{ ml l}^{-1}$ , Nishida, 2002). The high mixing coefficients for the South China Sea probably results from deep sea penetration of oxygen into pore waters (Rutgers van der Loeff, 1990) and high dissolved oxygen levels in the water column. Higher dissolved oxygen in pore waters facilitates the conversion from the particulate selenium to dissolved organic selenide. The higher concentration of selenium in pore waters derives from the high mixing coefficient in the South China Sea sediments.

### 3.3 Estimation of benthic fluxes at sediment-water interface

The concentration gradients of dissolved constituents at the sediment-water interface support diffusional transport. The diffusion of selenium from sediments into sea water occurs because their concentrations in pore waters of surface layers are higher than those in overlying sea water. The upward diffusive flux, in terms of the *benthic flux*, can be basically calculated through Fick's first law. In this study, the following equation was used, whereby the molecular diffusion coefficient in sea water could be substituted by the diffusion coefficient of dissolved species in the bulk sediment

(Berner, 1980; Aller *et al.*, 1985; Masuzawa, 1987);

$$F = -\phi D_{sed} \left( \frac{\partial C}{\partial z} \right) \quad (1)$$

where,  $F$  = flux,  $\phi$  = porosity,  $D_{sed}$  = diffusion coefficient in bulk sediment,  $D_{sw}$  = molecular diffusion coefficient in sea water media,  $C$  = pore water concentration, and  $z$  = depth in core.

$$D_{sed} = -\phi^{n-1} D_{sw} \quad (2)$$

$$F = -\phi^n D_{sw} \left( \frac{\partial C}{\partial z} \right)_{z=0} \quad (3)$$

It was assumed  $n$  was equal to 3 in this study (Masuzawa, 1987). Then, the diffusive flux was estimated by the following equation.

$$F = -\phi^3 D_{sw} \left( \frac{\partial C}{\partial z} \right)_{z=0} \quad (4)$$

$D_{sw}$  values for  $\text{SeO}_4^{2-}$  were estimated from the values of molecular diffusion coefficients in pure water using the ratio of viscosities with the temperature and salinity of pure water and sea water (Li and Gregory, 1974). Temperature and salinity of the bottom water at each station obtained by ordinary hydrographic observation are given in Table 2, along with the values of  $D_{sw}$  estimated for pore water constituents. The porosity of sediments was calculated from the water content, assuming the particle density was  $2.5 \text{ g cm}^{-3}$ . The concentration gradient at the interface was obtained from the differential derivative at  $z = 0 \text{ cm}$  for the regression curve of  $C$  as a function of  $z$ , assuming the initial condition,  $C_0$ , to be the concentration in the sea water overlying the core. Otherwise,  $\partial z$  was set at  $0.25 \text{ cm}$ , as the mid-depth of the first  $0-0.5$

Table 2 Estimation of the upward diffusive flux of selenium as selenate

Station	Temp (°C)	Salinity	Depth (m)	Bottom water (nM)	Gradient	Pore water (nM)	Porosity	$D_{sw}$ ( $\text{cm}^2 \text{yr}^{-1}$ )	$\partial C/dz$ ( $\text{pmol cm}^{-4}$ )	-Flux of selenate ( $\mu \text{g cm}^{-2} \text{yr}^{-1}$ )
					concentration at interface (nM)					
St.13	10.141	34.461	1881	0.50	10.1	19.2	0.8430	191	22.0	0.17
St.18	2.462	34.621	4251	0.53	26.6	104	0.9000	147	112	0.88

cm interval of the core sampled, and  $\partial C$  was substituted for the measured concentration difference in the overlying water preserved in the core barrel relative to that in the pore water of the first interval. The benthic fluxes calculated for selenium as selenate are summarized in Table 2; the estimated fluxes of selenium for St.13 and 18 were  $0.174$  and  $0.884 \mu \text{g cm}^{-2} \text{yr}^{-1}$ , respectively. These calculated fluxes were higher than the values of  $0.009 \mu \text{g cm}^{-2} \text{yr}^{-1}$  of St. Laurence Estuary (Takayanagi and Belzile, 1988) and  $0.009 \mu \text{g cm}^{-2} \text{yr}^{-1}$  of fresh water sediment (Belzile et al., 2000). The difference in the benthic flux can in part be attributed to the character of surface sediment. The diffusive flux values of dissolved selenium of the silty clay and/or silty clay with volcanic ash sediments were higher than the red-clay and calcareous ooze sediments. In addition, the mixing coefficients also affect the benthic fluxes.

## Conclusion

Selenium species, selenite, selenate and organic selenide in pore waters were simultaneously determined, and the total selenium concentrations in the sediment were also determined. The selenium accumulation rates for the Sulu Sea and the South China Sea were  $1.16$  and  $0.21 \text{ mg cm}^{-2} \text{yr}^{-1}$ , respectively. This may be due to the difference between the primary production of two sea area. The upward diffusive fluxes were calculated by using Fick's

first law. The estimated fluxes of dissolved selenium as selenate for the Sulu station St.13 and the South China Sea station St.17 were  $0.174$  and  $0.884 \mu \text{g cm}^{-2} \text{yr}^{-1}$ , respectively. These values were 20 – 100 times higher than the estuary and fresh water sediments

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