

## Concentrations of bromide and chloride ions and their relationships with salinity in the central region of the ROPME Sea Area

A. OTSUKI<sup>1</sup>, K. NAGAOKA<sup>1</sup>, S. HASHIMOTO<sup>1</sup>, R. TSUJIMOTO<sup>2</sup>, T. SENJYU<sup>3</sup>  
and Y. KOIKE<sup>4</sup>

<sup>1</sup>*Tokyo University of Fisheries, Department of Ocean Sciences,  
5-7 Konan 4, Minato-ku, Tokyo 108-8477, Japan*

<sup>2</sup>*Toyama Prefectural Fisheries Research Institute,  
2373 Takatsuka, Namerikawa, Toyama 936, Japan*

<sup>3</sup>*National Fishery University, Department of Fishery Science and Technology,  
2-7-1 Nagatahonmachi, Shimonoseki Yamaguchi 759-65, Japan*

<sup>4</sup>*Tokyo University of Fisheries, Research and Training Vessels,  
5-7 Konan 4, Minato-ku, Tokyo 108-8477, Japan*

**Abstract**—The concentrations of chloride and bromide ions in seawater samples from the central region of the Regional Organization for the Protection of the Marine Environment (ROPME) Sea Area were determined by ion chromatography after 100-fold dilution with ultra-pure water. The calibration curves were highly linear between 0 and 500 mg l<sup>-1</sup> for chloride and between 0 and 1 mg l<sup>-1</sup> for bromide with correlation coefficients for both of greater than 0.999. The relative standard deviations at salinity 39.861 were ±0.53% for chloride ion and ±0.91% for bromide ion ( $n = 5$ ), respectively.

The concentrations of chloride and bromide ions in open seawater in the central region of the ROPME Sea Area ranged from 21.70 to 23.56 g kg<sup>-1</sup> with an average value of 22.20 g kg<sup>-1</sup> and from 76.4 to 81.4 mg kg<sup>-1</sup> with an average value of 78.3 mg kg<sup>-1</sup>, respectively, while the salinity range was from 39.551 to 42.314 PSU. These average concentrations were 14.7% higher for chloride ion and 16.3% higher for bromide ion than those in ocean water of average salinity, 35 PSU.

An excellent linear relationship between salinity and chloride ion concentration in the salinity range to 42.314 PSU with correlation coefficient of 0.981 was confirmed in open seawater samples in this region. The ratios of bromide to chloride were distributed nearly normal with an average value of 0.00353, which is the highest value reported for the oceans and seas with one exception, the Red Sea.

### INTRODUCTION

The ROPME Sea Area, which does not have a large river water input except for the Shatt al-Arab River, is located in the desert zone in the Middle East, and evaporation there far exceeds freshwater input (Abuzinada and Krupp, 1994). Although some authors have reported salinities (38–42 PSU) in open seawater of the ROPME Sea Area higher than the average salinity of 35 for the world's oceans



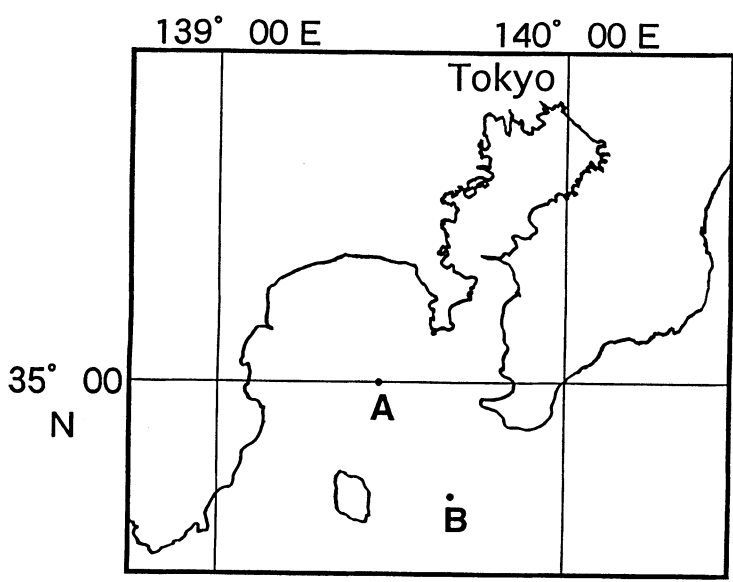
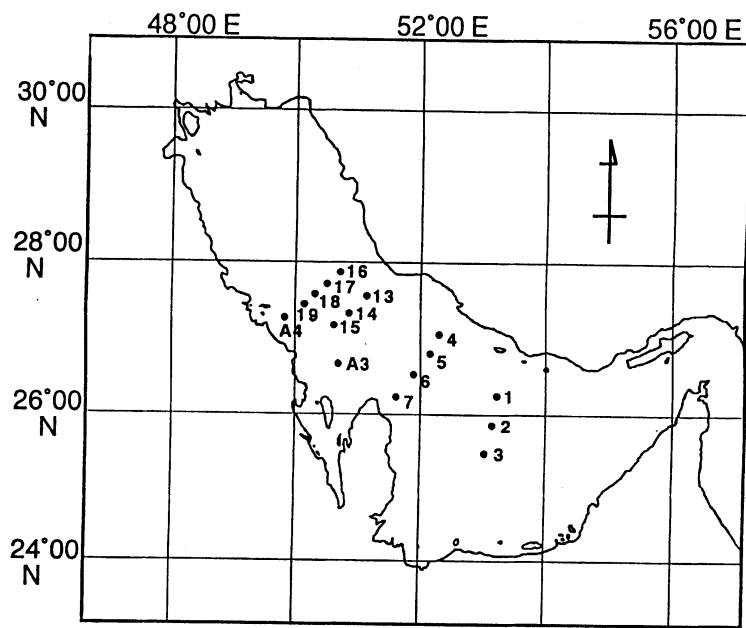


Fig. 1. Sampling stations in the ROPME Sea Area (upper) and in Sagami Bay, Japan (lower).

with a IonPac AG4A-SC column (4 mm I.D. × 25 cm in length) connected to a guard column, IonPac AG4A (4 mm I.D. × 5 cm in length), was used. Detection was via a conductivity meter. Data was acquired with a Shimadzu Chromatopak C-R6A integrator.

#### *Analytical conditions*

The mobile phase was a 1.8 mM Na<sub>2</sub>CO<sub>3</sub>-1.7 mM NaHCO<sub>3</sub> solution. The flow rate was 1.0 ml min<sup>-1</sup> and injection volume was 25 μl. The sensitivities of the conductivity meter were set at 300 μS for chloride ion and 3 μS for bromide ion, respectively. Calibration curves were prepared with standards between 0 and 500 mg l<sup>-1</sup> for chloride ion and between 0 and 1 mg l<sup>-1</sup> for bromide ion, respectively.

#### *Analytical method*

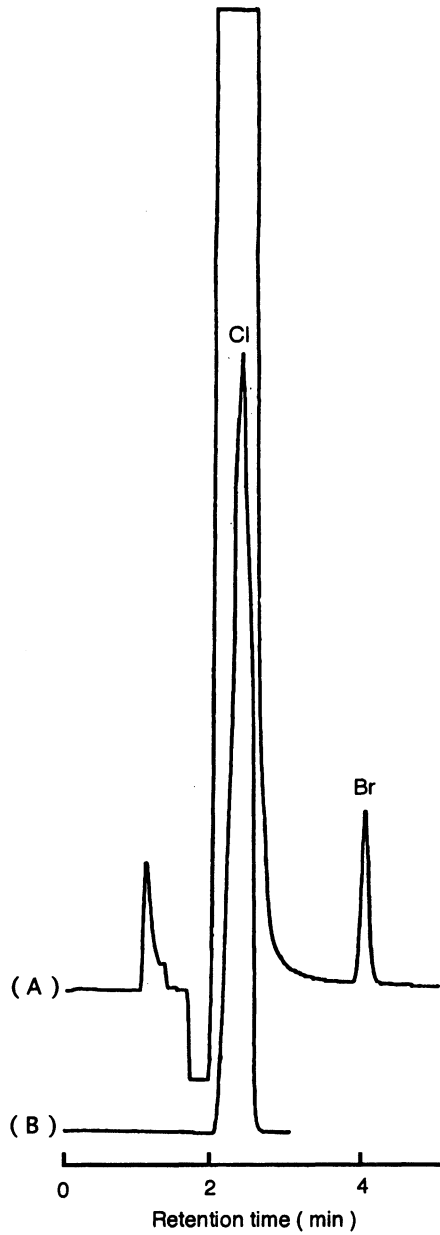
After 100-fold dilution of each seawater sample with pure water, 25 μl of the diluted samples were automatically injected into the ion chromatograph and the area of each chloride and bromide ion peak was measured. Each sample was analyzed in triplicate. After the determination of both ions on a weight per volume basis, their concentrations were converted to a weight basis using the density at each sampling depth.

Salinity was determined with a Guildline AUTOSAL. Values from this salinometer were used to calibrate the CTD salinity value.

## RESULTS AND DISCUSSION

The useful chromatograms for both chloride and bromide ions after 100-fold ions dilution were achieved by changing detection sensitivities (Fig. 2). When a low sensitivity of 300 μS for full scale was used to determine the concentration of chloride ion in diluted seawater, only one peak, for chloride ion was observed on the ion chromatogram, but when the sensitivity was elevated to 3 μS, a sharp peak for bromide ion appeared after the large peak for chloride ion. These results confirm that 100-fold dilution of seawater samples with pure water is appropriate for ion chromatographic determination of both ions in the seawaters of this region. Calibrations were highly linear between 0 and 500 mg l<sup>-1</sup> for chloride ion and between 0 and 1 mg l<sup>-1</sup> for bromide ion with correlation coefficients for both of greater than 0.999. The relative standard deviations at salinity 39.861 were ±0.53% for chloride ion and ±0.91% for bromide ion (*n* = 5), respectively. Recoveries of additions of 10.0 mg chloride and 0.10 mg bromide ions to 100 ml of 100-fold dilution of seawater sample at ST14-40 m were 99.92% for chloride ion and 99.59% for bromide ion, respectively. The bromide ion peak was confirmed by the increased one caused by this addition of bromide.

The concentrations of chloride and bromide ions in open seawaters of the central region of the ROPME Sea Area ranged from 21.70 to 23.56 g kg<sup>-1</sup> with an average value of 22.20 g kg<sup>-1</sup> and from 76.4 to 81.4 mg kg<sup>-1</sup> with an average value of 78.3 mg kg<sup>-1</sup>, respectively, while the salinity range was from 39.551 to 42.314 PSU (Table 1). These average concentrations were 14.7% and 16.3% higher than



Sample ST 17-40m  
Range  $3 \mu\text{S}$  (A)  
Range  $300 \mu\text{S}$  (B)

Fig. 2. Ion chromatograms of chloride and bromide ions in a diluted seawater sample achieved by changing the detection sensitivity of the conductivity meter.

Table 1. The concentrations of chloride and bromide ions in open seawaters at some sampling stations in the central region of the ROPME Sea Area.

Station	Latitude N	Longitude E	Sampling depth (m)	Temperature (°C)	Salinity (PSU)	Chloride ion (g kg <sup>-1</sup> )	Bromide ion (mg kg <sup>-1</sup> )
ST-2	25° 54.40'	53° 07.90'	4	24.40	39.596	21.98	76.4
			8	24.42	39.596	21.98	78.8
			20	24.37	39.596	21.98	79.5
			30	24.40	39.629	21.98	78.8
			40	24.43	39.642	21.98	78.8
			50	24.51	39.683	21.98	78.8
			59	24.52	39.689	21.98	78.8
ST-6	26° 27.90'	51° 48.50'	5	23.70	39.700	21.86	78.7
			10	23.69	39.698	22.05	79.5
			20	23.62	39.695	22.22	76.4
			30	23.60	39.698	22.23	77.1
			41	22.19	41.218	22.99	79.3
ST-7	26° 13.00'	51° 35.20'	4	23.05	40.000	22.23	77.9
			9	23.04	40.000	22.23	77.1
			23	21.12	42.314	23.56	81.4
ST-15	27° 09.80'	50° 41.70'	4	23.26	39.943	22.45	80.2
			10	23.21	39.942	22.45	80.2
			20	23.20	39.939	22.26	79.2
			30	23.21	39.953	22.45	79.5
			40	23.17	39.953	22.45	79.5
			50	23.17	39.960	22.26	80.2
			62	23.20	40.198	22.45	80.2
ST-18	27° 36.00'	50° 17.80'	4	23.18	40.147	22.26	77.9
			10	23.13	40.145	22.04	77.9
			20	23.14	40.146	22.04	77.9
			30	23.14	40.147	22.04	78.7
			40	23.13	40.152	22.04	77.9
			50	23.13	40.170	22.04	77.9
			60	23.15	40.186	22.04	77.9

the 19.354 g kg<sup>-1</sup> and 67.3 mg kg<sup>-1</sup> of chloride and bromide ions concentrations, respectively, in ocean water of average salinity, 35 PSU. In contrast, in Sagami Bay the concentrations of chloride ion ranged from 18.64 g kg<sup>-1</sup> at 1,200 m depth to 18.86 g kg<sup>-1</sup> at 100 m depth, and that of bromide ion from 64.9 mg kg<sup>-1</sup> at 2,000 m depth to 65.8 mg kg<sup>-1</sup> at 100 m depth, respectively, 18–20% lower than those in the central region of the ROPME Sea Area.

The frequency distribution of bromide to chloride ratios in open seawaters of this region is nearly normal distribution (Fig. 3), with a maximum value between 0.003525 and 0.00355. The mean value, 0.00353, was higher than any other values for the world oceans and seas shown in Table 2 (Morris and Riley, 1966).

Figures 4(a), 4(b) and 4(c) show three examples of vertical distributions of the bromide to chloride ratio at ST-2, ST-6 and ST-14, suggesting that the behavior of bromide ion in this region is not always identical to the same as that of chloride ion. Although the relationship between salinity and chloride ion concentrations (Fig. 5) was completely linear, that between chloride and bromide

Table 2. Concentrations of bromide ion in world sea waters.

Reference	Ocean or Sea etc.	Br(g/kg)[for S=35‰]	Br/Cl
BERGLUND(1885)	North	0.0638-0.0665	0.00330-0.00334
	Atlantic	0.0652-0.0660	0.00337-0.00341
	Gulf of Mexico	0.0660	0.00341
	Mediterranean	0.0663	0.00343
	Adriatic	0.0660	0.00341
MAKIN(1898)	Atlantic	0.0628	0.00325
WINKLER(1916)	Adriatic	0.0670	0.00347
CAMERON(1922)	Departure Bay	0.0693	0.00358
VASIL'EV(1937)	Japan	0.0643	0.00333
RATMANOFF(1937)	Bering	0.0668	0.00345
MIYAKE(1939)	W.Pacific	0.0640	0.0033
THOMPSON and KORPI(1942)	N.E.Pacific	0.0673	0.00348
	Antarctic	0.0667	0.00345
	Bering	0.0670	0.00347
MATIDA and YAMAUCHI(1951)	Japan	0.0670	0.00347
HASLAM and GIBSON(1950)	British Coastal Waters	0.0667	0.00345
THIS STUDY(1994)	ROPME Sea Area*	0.0783	0.00353
	Sagami Bay Japan*	0.0650	0.00348

\*ROPME Sea Area {S = 39.395–42.314‰}, Sagami Bay Japan {S = 34.266–34.586‰}.  
 Morris, A. W. and J. P. Riley, 1966.

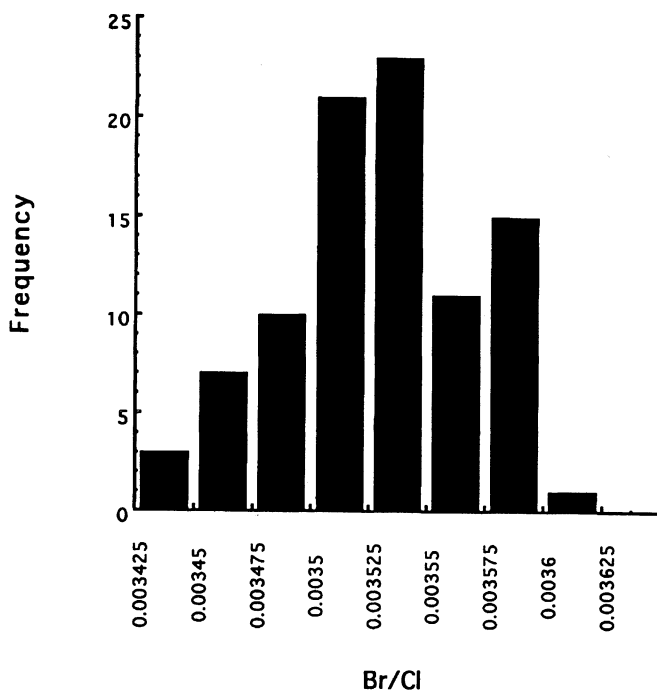


Fig. 3. Histogram of bromide to chloride ratios in open seawaters of the central region of the ROPME Sea Area.

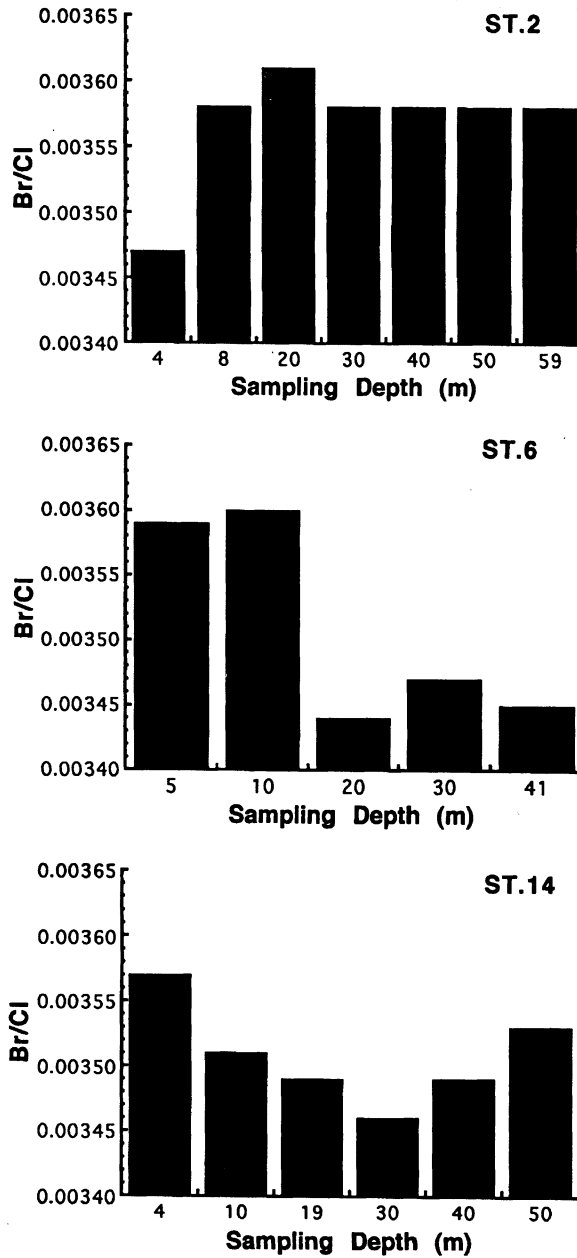


Fig. 4. Vertical distributions of bromide to chloride ratios at ST-2 (a), ST-6 (b) and ST-14 (c).

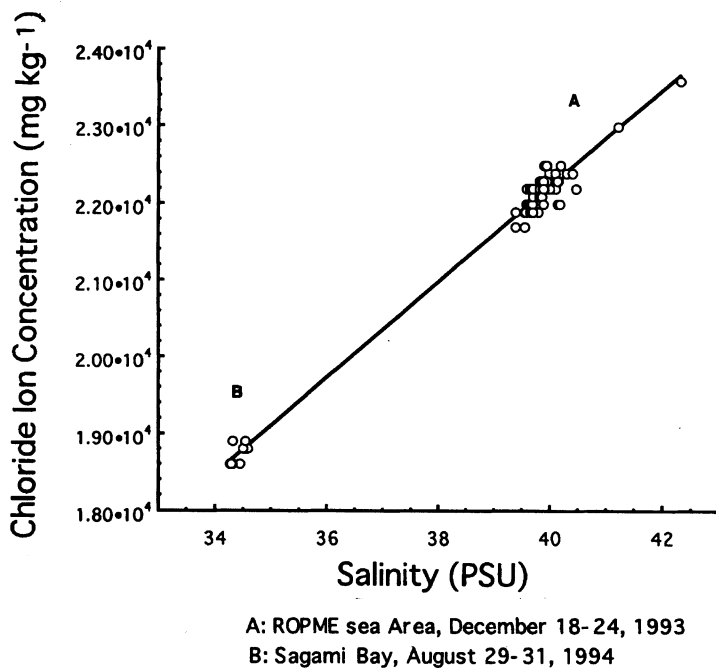


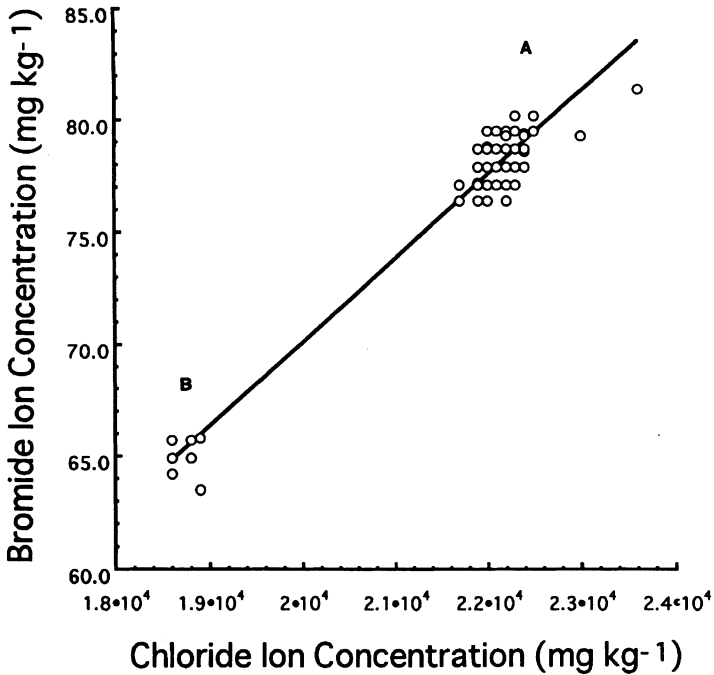
Fig. 5. Relationship between salinity and chloride ion concentration in the central region of the ROPME Sea Area.

ions concentrations (Fig. 6) deviated from linearity near the chloride ion concentration of  $23.00 \text{ g kg}^{-1}$  for unknown reasons. These results suggest that the ratio of chloride ion concentration to salinity as well as the density may be tracers of water masses in the ROPME Sea Area.

#### CONCLUSIONS

The present study was the first to report the precise concentrations of chloride and bromide ions in open seawater of the central region of the ROPME Sea Area using ion chromatography. Chloride ion concentration ranged from  $21.71$  to  $23.56 \text{ g kg}^{-1}$  with an average of  $22.20 \text{ g kg}^{-1}$  and bromide ion ranged from  $76.4$  to  $81.4 \text{ mg kg}^{-1}$  with an average of  $78.3 \text{ mg kg}^{-1}$ . We confirmed the linear relationship between chloride ion concentrations and salinity up to salinities of  $42.314 \text{ PSU}$ .

The ratios of bromide to chloride ions in open seawaters of the central region of the ROPME Sea Area had a nearly normal frequency distribution with an average value of  $0.00353$ , which was the highest value reported for the oceans and



A: ROPME Sea Area, December 18-24, 1993

B: Sagami Bay, August 28-31, 1994

Fig. 6. Relationship between chloride and bromide ions in the central region of the ROPME Sea Area.

seas with the one exception of the Red Sea.

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#### REFERENCES

- Abdulaziz A. H. and Krupp, F. (1994). The Arabian Gulf environment and the consequences of the 1991 oil spill. *Cour. Forsch.-Inst. Senckenberg*. 166, 3-10.
- Brewer, P. G. and Dyrssen, D. (1985). Chemical oceanography of the Persian Gulf. *Prog. Oceanogr.* 14, 14-55.
- Morris, A. M. and Riley, J. P. (1966). The bromide/chlorinity and sulphate/chlorinity ratio in seawater. *Deep-Sea Res.* 13, 699-705.
- Samra, M. I. El (1988). Chemical observations in the Arabian Gulf and the Gulf of Oman. *Arab Gulf J. Scient. Res. Math. Phys. Sci.*, A6, 204-215.