

On Fluoride, Bromide and Iodide in the Southwestern Indian Ocean Sector of the Southern Ocean

Francisca P. De Souza¹ and R. Sen Gupta¹

ABSTRACT

In seawater, the average fluoride concentration and fluoride/chlorinity ratio were 1.31 ± 0.003 mg/l and $(6.67 \pm 0.02) \times 10^{-5}$ respectively. Samples of the deep water upto a depth of 4000 m when analysed for fluoride gave no indication of any anomalously high concentrations and the effect of dissolution at or from the bottom was ruled out. Bromide content (average 68.08 mg/l) and chlorinity varied in a parallel manner and a rather constant Br/Cl ratio of 0.00347 was established. The iodide concentrations varied irregularly with depth (average 1.011 mg/l with I/Cl 0.56×10^{-6}), the iodide content being greater in the upper and bottom layers at all stations. While fluoride and bromide mainly influenced the physical properties of seawater, the importance of iodide lay in the chemical and biological fields.

INTRODUCTION

The use of salinity in the calculations of density and current velocity in seawater assumes that the relative proportions of the major seawater constituents are constant in space and time. This assumption is approximately true, but variations have been reported and they are probably real (Carritt and Carpenter, 1959). However, the magnitude and, in some cases, the reality of the variations have not been well established because of conflicting results reported by different workers (Culkin, 1965). Until recently, it has been a matter of some debate as to whether fluoride is a conservative component of seawater or not (Greenhalgh and Riley, 1963; Riley, 1965; Brewer *et al.*, 1970; Bewers *et al.*, 1973). It has been found that diverse conditions prevailing in the Bay of Bengal, Andaman Sea and Arabian Sea affect the behaviour of fluoride vis-a-vis chlorinity (Sen Gupta *et al.*, 1978; Noronha *et al.*, 1981; De Souza, 1982). These authors felt that it was more appropriate to describe fluoride as a semi-conservative constituent. The distribution of bromide was, in general, closely related to that of salinity because it tended to behave conservatively (Culkin, 1965; Morris and Riley, 1966; De Souza and Sen Gupta, 1981; De Souza, 1982). Iodide, a minor constituent, on the other hand, was investigated in the Arabian Sea and found to show non-conservative characters being affected by chemical and biological processes (De Souza, 1982).

These prompted us to pay renewed attention to halide studies based on the data from samples collected during the First Indian Expedition to Antarctica on board M. V. *Polar Circle* during the southern summer of 1981-82.

MATERIALS AND METHODS

Samples were collected from standard hydrographic casts using 2 litre Niskin bottles. In all, sixteen stations were worked (Fig. 1) for the present analysis. Since fluoride anomalies are reported at depths greater than 2000 m in the Northwest Atlantic, water samples down to 4000 m were collected to find out the anomalies, if any. These samples were stored in well-sealed polyethylene bottles and analysed several weeks later in the shore laboratory.

Fluoride was estimated photometrically by the lanthanum-alizarin complexone method of Greenhalgh and Riley (1961). The determination included any particulate or colloidal fluoride which would react with the alizarin complexone reagent, because the seawater was not filtered. Correction

¹ National Institute of Oceanography, Dona Paula, Goa-403 004

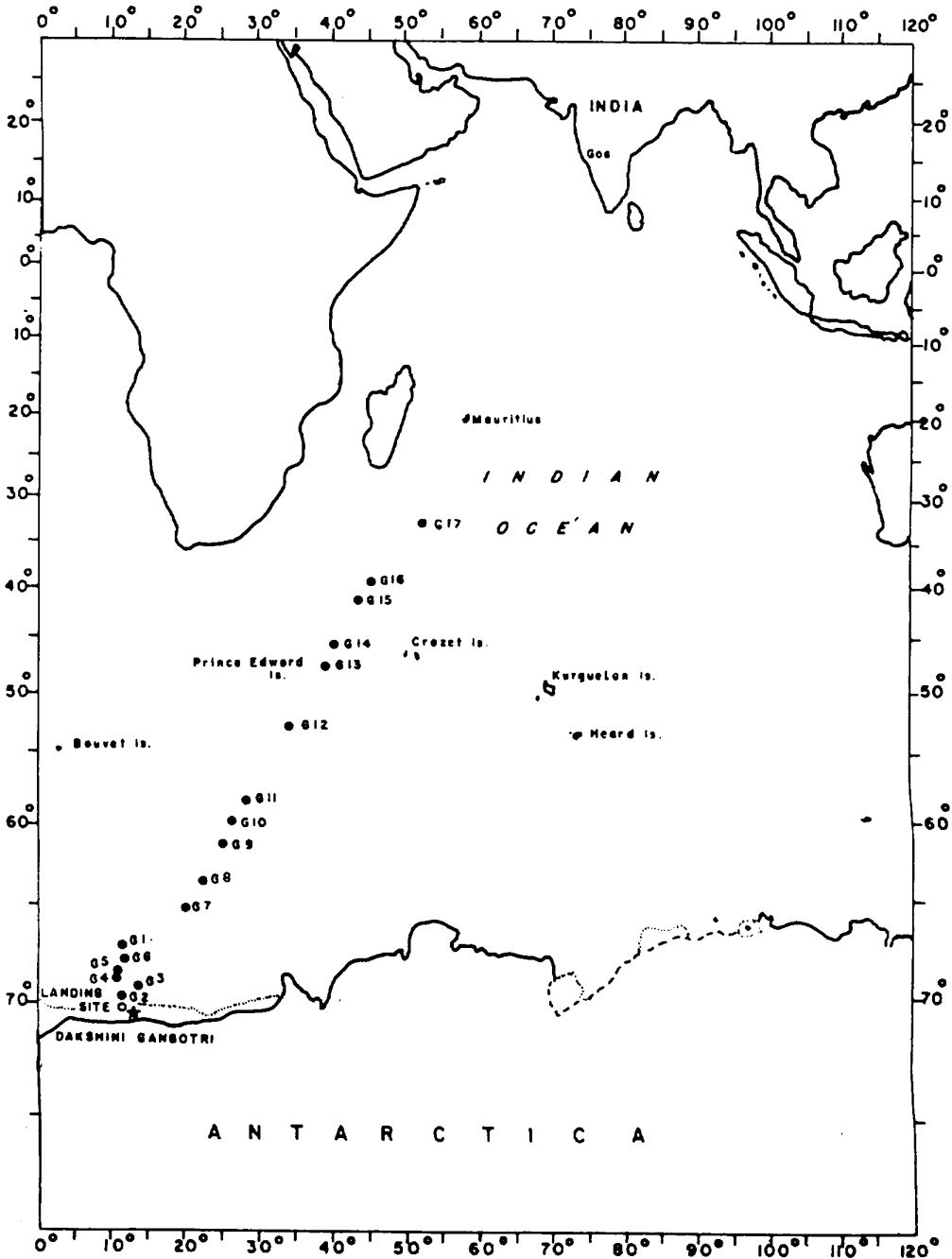


Fig. 1 : Station Locations

was applied to the absorbances in the water to account for the salt error of the analysis. Bromide was estimated by the spectrophotometric method of Saenger (1972). Absorbance at 650 nm was used to allow for slight differences in the turbidity of the samples, and subtracted from the absorbance at 400 nm. Iodide was measured employing the iodide ion-selective electrode. Chlorinity was based on measurements using an Autosal inductive salinometer with a sensitivity of $\pm 0.003\%$. The coefficient of variation determined from the repeats of a few samples was $\pm 0.77\%$ for fluoride; $\pm 1.52\%$ for bromide and $\pm 3.22\%$ for iodide.

RESULTS AND DISCUSSION

Fluoride

Fluoride is generally considered to be a major component of seawater, being present in the oceans at a concentration of about 1.3 mg/kg at 35‰ salinity and bearing a ratio of approximately 6.7×10^{-5} to chlorinity. To have a general idea of distribution of fluoride and fluoride/chlorinity ratio in the study area, the results were pooled depthwise and the average F^- and F/Cl ratios were calculated at each depth. The overall average fluoride concentration of 1.31 ± 0.003 mg/l and F/Cl ratio of $(6.67 \pm 0.02) \times 10^{-5}$ were obtained. These values are in close agreement with the mean F^- concentration obtained by Sen Gupta *et al.*, (1978) in the Northern Indian Ocean and the average F/Cl ratio observed by De Souza (1982) in the Arabian Sea.

To study spatial and depthwise variations of fluoride concentration and F/Cl ratio, the stations were clustered in three different regions, eg., south of 65°S (Stn. G1-G6), 52°—65°S (Stn. G7-G12) and 39°—47°S (Stn. G13-G16). These divisions would, very broadly, indicate the Antarctic (Polar) Divergence, Antarctic Convergence and Sub-Tropical Convergence regions of the area of our observations. To delineate the water masses we have further sub-divided the values into 0–100 m, 125–500 m, 600–1000 m, 1100–2000 m and > 2000 m depth ranges. Average values of fluoride and F/Cl ratio in these depth ranges are presented in Table 1.

TABLE 1

Average fluoride and fluoride/chlorinity ratio at different depth levels and regions

Station	Area	0-100 m		125-500 m		600-1000 m		1100-2000 m		> 2000 m	
		F (mg/l)	(F/Cl) $\times 10^{-5}$	F (mg/l)	(F/Cl) $\times 10^{-5}$	F (mg/l)	(F/Cl) $\times 10^{-5}$	F (mg/l)	(F/Cl) $\times 10^{-5}$	F (mg/l)	(F/Cl) $\times 10^{-5}$
G1-G6	Antarctic Divergence	1.30	6.89	1.30	6.84	1.30	6.83	1.32	6.86	—	—
G7-G12	Antarctic Convergence	1.29	6.87	1.30	6.82	1.31	6.85	1.31	6.83	—	—
G13-G16	Sub-tropical Convergence	1.32	6.92	1.32	6.92	1.31	6.86	1.32	6.86	1.33	6.92

Fluoride concentrations in the surface layers increase northwards from the Antarctic coast. Lower values in the polar divergence and Antarctic convergence regions are caused by the melting of ice. Similarity in the fluoride concentrations in different depth ranges might indicate same or identical sources of origin for the watermasses. But variations in F/Cl ratio, indicating chlorinity variations at these depths would indicate otherwise. Higher values for both fluoride and F/Cl concentrations at depths over 1000 m probably indicate the penetration of North Atlantic Deep Water in the Indian Ocean region of the Southern Ocean, as has been suggested by Deacon (1937). High fluoride and high F/Cl ratio in the upper 500 m in the Sub-Tropical convergence region indicate the predominance of Indian Ocean surface water.

The averages of F⁻ (mg/l) and F/Cl ratios with standard errors for the whole watermass in the three areas are presented in Table 2. The table indicates that in the depth range of our observations there is hardly any variation of these components from the accepted concepts of their normal behaviour in the oceans. In other words, no abnormal behaviour, due to geochemical factors, are evident.

TABLE 2
Average fluoride and fluoride/chlorinity ratio in different regions

AREA	F ± Std. error	F/Cl ± Std. error × 10 ⁻³
Antarctic Divergence	1.30 ± 0.003	6.86 ± 0.01
Antarctic Convergence	1.30 ± 0.003	6.85 ± 0.02
Sub-Tropica Convergence	1.32 ± 0.003	6.91 ± 0.01

From observations of fluoride concentrations from 0-20‰ chlorinity, Kullenberg and Sen Gupta (1973) deduced the following relations between the two variables:

$$F \text{ (mg/l)} = 0.166 + Cl^2 / (36.7 + 0.755 Cl^2) \quad (1)$$

To test our values we calculated the depthwise averages for all the observed values of chlorinity and fluoride. These, when fitted to eq. 1, gave the results as in Table 3.

Kullenberg and Sen Gupta (1973) observed an asymptotic relation for eq. 1 above about 19.2 ‰ chlorinity. The calculated values of fluoride in Table 3 should confirm this. The difference between the observed and calculated values of fluoride varies from 0 to -0.03. a not very significant difference, considering the sources of error which might influence the analysis and the calculations.

TABLE 3
Observed and calculated values at different depths and chlorinity intervals

Depth m	Cl ‰	F _{obs}	F _{calc}	F _{obs} - F _{calc}
0	18.93	1.31	1.33	- 0.02
50	18.86	1.30	1.33	- 0.03
100	19.02	1.30	1.33	- 0.03
125	19.04	1.30	1.33	- 0.03
200	19.09	1.31	1.33	- 0.02
250	19.17	1.32	1.33	- 0.01
300	19.26	1.33	1.33	± 0
500	19.12	1.31	1.33	- 0.02
750	19.17	1.32	1.33	- 0.01
1000	19.18	1.31	1.33	- 0.02
1250	19.18	1.31	1.33	- 0.02
1500	19.18	1.31	1.33	- 0.02
2000	19.19	1.31	1.34	- 0.03
3000	19.25	1.34	1.34	± 0.0
4000	19.19	1.32	1.34	- 0.02

Concentrations of fluoride at the surface waters at stations G1 and G2 will be most influenced by the melting of ice and as such should show a deficit. The deficit, thus, becomes 0.02 and 0.03. This would indicate that meltwater from ice should have 0.136 to 0.146 mg/l of fluoride, as compared to 0.166 for river water, used to deduce eq. 1.

Based on the fluoride concentrations, the entire water column can be divided into three distinct layers (Fig. 2), (i) surface layer (0—100 m), (ii) middle layer (100—2000 m) and (iii) bottom layer (2000—4000 m). In the surface layer, the fluoride concentrations remained constant and did not follow the trend of dissolved oxygen. In the middle layer the distribution was irregular (1.29—1.33 mg/l). However, a similar trend as noted by Sen Gupta *et al.* (1978), Noronha *et al.* (1981), De Souza (1982) and Naik and Dias (1982) was observed i.e. in the zone of comparatively low oxygen concentrations fluoride maintained constant (1.31 mg/l) values (1000—2000 m). In the deeper layer, the concentrations increased compared to the middle layer (1.33 mg/l). The small variations in fluoride and its ratio with chlorinity in all these layers are attributed to changes in salinity and dissolved oxygen concentrations. This is confirmed by the fact that fluoride can be removed in the presence of low oxygen and redissolved when oxygen concentrations increase (Kullenberg and Sen Gupta, 1973), though the upper layer did not show this pattern.

(ii) Bromide

Bromide in the oceans is one of its major and conservative components. Seawater at 35 ‰ salinity holds 67.3 mg/kg bromide maintaining a remarkably constant ratio of 34.73×10^{-4} (Culkin, 1965), but some variations may exist (Morris and Riley, 1966). From theoretical studies Sillén (1961) concluded that at the pH and pE of seawater bromine can be present only as bromide ion.

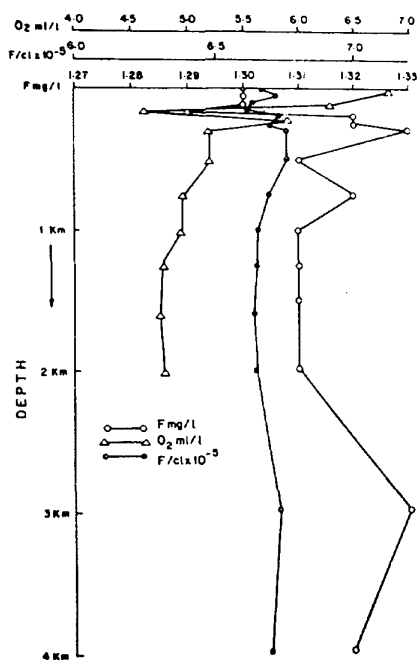


Fig. 2 : Depth profiles of average values of fluoride (mg/l) oxygen (ml/l) and fluoride/chlorinity ratio

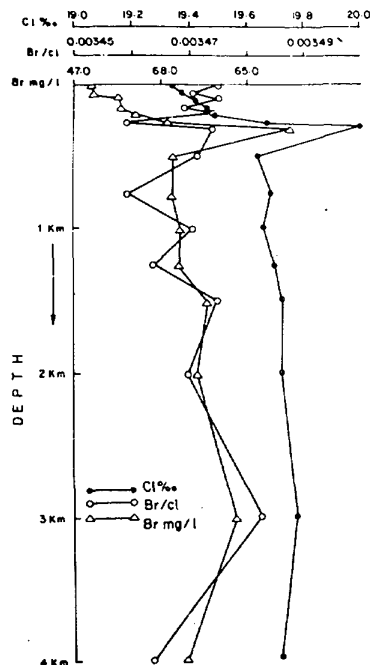


Fig. 3 : Depth profiles of average values of bromide (mg/l), chlorinity and bromide/chlorinity ratio

On examining the bromide distribution it was clear that a remarkably steady relationship existed between the bromide content and chlorinity of seawater (Fig. 3). Bromide showed a conservative behaviour as it bore a fairly constant ratio to chlorinity of 0.00347. A ratio of 0.00345 for Antarctic Ocean has been obtained by Thompson and Korpi (1942). Elsewhere, a ratio of 0.00347 for Antarctic Ocean was recorded (Wright, 1978). A fairly constant value of 0.00347 was obtained by De Souza and Sen Gupta (1981) and De Souza (1982) in the Arabian Sea. The present ratio is in excellent agreement with these values.

An attempt has been made to study the variations in bromide and Br/Cl ratio spatially and depthwise as was done for fluoride earlier. Table 4 indicates an increase of bromide away from the

TABLE 4

Average bromide and bromide/chlorinity ratio at different depth levels and regions

Station	Area	0-100 m		125-500 m		600-1000 m		1100-2000 m		> 2000 m	
		Br (mg/l)	(Br/Cl) × 10 ⁻⁴	Br (mg/l)	(Br/Cl) × 10 ⁻⁴	Br (mg/l)	(Br/Cl) × 10 ⁻⁴	Br (mg/l)	(Br/Cl) × 10 ⁻⁴	Br (mg/l)	(Br/Cl) × 10 ⁻⁴
G1-G6	Antarctic Divergence	67.30	34.68	68.44	34.71	68.14	34.57	68.14	34.60	-	-
G7-G12	Antarctic Convergence	67.22	34.79	68.00	34.70	68.43	34.76	68.48	34.72	-	-
G13-G16	Sub-Tropical Convergence	67.94	34.71	68.09	34.73	68.19	34.78	68.40	34.74	68.48	34.71

Antarctic coast. It becomes obvious that concentrations in the upper layer at the Polar divergence and Antarctic convergence are influenced by the basal melting of ice during the austral summer. An increase in depth has been observed in all the watermasses with an insignificant variation in the Br/Cl ratio. This indicates the conservative character of bromide in seawater as it increases proportional to the chlorinity. However, the increase in bromide concentration does not appear to be very real as the difference is within the coefficient of variation of our analytical method. In other words, the average concentration of bromide in all the regions (Table 5) are almost the same corroborating the conclusion of Culkin (1965). The overall average bromide concentration is 68.08 mg/l with a Br/Cl ratio of 0.00347. In general, the deeper layers were enriched with bromide as compared to the surface layers. The high contents were associated with high salinities. Thus bromide and chlorinity showed a parallel behaviour.

TABLE 5

Average bromide and bromide/chlorinity ratio in different regions

	Br ± std. error	(Br/Cl ± std. error) × 10 ⁻⁴
Antarctic Divergence	68.00 ± 0.11	34.64 ± 0.02
Antarctic Convergence	68.03 ± 0.09	34.74 ± 0.02
Sub-tropical Convergence	68.22 ± 0.10	34.73 ± 0.01

(iii) Iodide

Iodine occurs in the oceans as iodate and iodide (Sugawara and Terada, 1958). Organic iodine may also be present in minute quantities (Lovelock, Maggs and Wade, 1973; Truesdale, 1975). Iodate is the thermodynamically stable species, and if equilibrium were reached, the iodate to iodide ratio should be 10^{13.5} at the pH and pE of open oceanic waters (Sillén, 1961). However, observations show that a significant amount of iodide is usually present.

In the surface layers, iodide concentrations varied from 0.010 to 0.020 mg/l. These values were greater than those in the middle layer. Tsunogai and Sase (1969), on the basis of their laboratory studies, proposed that iodide can be produced by the enzymetic reduction of iodate, with nitrate reductase as the catalyst. In a later survey, Tsunogai and Henmi (1971) found that the levels of iodide in various surface waters in the Pacific can be qualitatively classified by their potential productivity. Wong and Brewer (1974) studied the behaviour of iodate and found that it behaved like the nutrients. These relationships suggest that the marine chemistry of iodide may be intimately related to biological activities. This explains the high iodide concentrations in surface waters. Wong and Brewer (1974) have observed low iodate concentrations in the surface layer which were caused by biological stripping of total iodine, loss of iodine to the atmosphere, or associated with the presence of high concentrations of iodide. These may also be the reasons for high concentrations of iodide at the surface. Elderfield and Truesdale (1980) showed a variable depletion of iodate and total iodine from the near-surface waters and a near constant value at depth. The depletion of total iodine (equivalent to $< 0.01-0.06 \mu\text{M}$ at 35‰S) was always smaller than the iodate depletion thus showing that a net interconversion of iodine species occurs.

At a few stations, we noticed that the surface values (0.008-0.015 mg/l) of iodide were lower than the sub-surface values (0.010-0.021 mg/l). The only possible way for iodide to decrease in seawater is by the photochemical oxidation of iodide to iodate. If this change does occur, it is only possible in the upper layer of the sea where oxygen is rich and illumination is sufficient (Sugawara and Terada, 1957). Another possible way for iodide to decrease in seawater is by the photochemical oxidation of iodide in the air. Low iodide in the surface at these stations may also reflect the low productivity in this region. The middle layer of the seawater is characterized by low iodide concentrations associated with low oxygen and high salinity. The bottom layers always showed higher iodide concentrations, and the highest observed concentration was 0.021 mg/l at 4000 m depth (Fig. 4). A similar feature was observed by Tsunogai (1971) in deep water, and three sources, are suggested for the production of iodide.

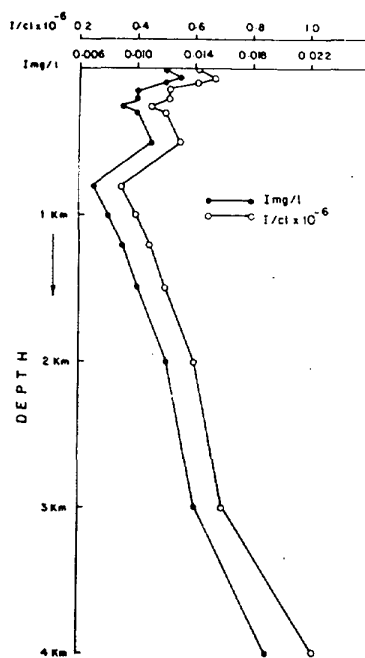


Fig. 4 : Depth profile of average values of iodide (mg/l) and iodide/chlorinity ratio.

First, it has been found that the concentration of iodide is generally larger in the deep water than in the surface waters. This indicates that iodide in the ocean is incorporated into organic matter at the surface and dissolved in the deep water after sinking as seston. This supplies iodide to the deep water. In the second place, the depth profile of iodate seemed to be inversely correlated with that of iodide. This indicated that iodide in seawater was formed *in situ* from iodate and vice versa. As the third source, the iodide is presumably found in the layer near or in the bottom due to higher concentration of iodide in the bottom water derived from the decomposition of organic matter, and from iodate reduction from unevenly distributed sources. The amount of iodide reduced from iodate on the bottom was found to be a few times greater than the amount of iodide supplied from the decomposition of organic matter in the deep water as estimated by Tsunogai (1971 b).

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