

# Chemical Studies on the Ice Shelf, in a Freshwater Lake and in a Polynya at Princess Astrid Coast, Dronning Maud Land, Antarctica

R. Sen Gupta<sup>1</sup> and S.Z. Qasim<sup>2</sup>

## ABSTRACT

Chemical characteristics such as salinity, temperature, dissolved oxygen, phosphate, nitrate, nitrite, silicate, calcium, magnesium, potassium, fluoride, bromide, iodide, iron, zinc, copper, manganese, nickel, cobalt, lead and cadmium were measured upto 5 meters in the ice shelf, in the surface waters of a freshwater lake in Antarctica and at several water depths in the polynya.

An increasing vertical gradient downwards in most of the constituents was found in the ice. This is probably because of the diffusion of salts in the ice and also a somewhat reducing condition of nitrate prevailing in the ice at depths. Surface concentrations of some elements in the ice appear to be influenced by the atmospheric transport and deposition. No significant difference was found in the constituents at some distance away from the shore.

Concentrations of most of the elements in the freshwater lake are largely regulated by the melted water coming from the glaciers and surrounding ice, leaching of materials from the rocks and the evaporation caused during the prolonged summer.

Concentrations of the heavy metals in the ice and in the lake and in a Himalayan glacier at varying heights were found to be of a similar order. These features indicate that both Antarctica and the high altitudes of the Himalayas have clean and unpolluted environment. Using these two as the southernmost and northernmost reference points, a watch can be maintained on the health of the Indian Ocean.

Hydrochemical studies of the polynya in Antarctica indicate that the surface layers are influenced by the melting of ice but an oceanic layer exists below 150 m depth. Chemical characteristics of the lower layers have much similarities with those of the deeper waters of the Southern Ocean. The height of the ice shelf was about 20 m above the sea. Particulate matter resulting from the melting of ice probably adds to the reserves of nutrients and heavy metals of the sea water.

## INTRODUCTION

Approximately 45% of the coastline of Antarctica is bordered by floating glacial ice sheets known as ice shelves (Carmack and Foster, 1975). These ice shelves undergo large seasonal changes in their size and volume. Satellite observations for 1973-1975 showed that the maximum cover in sea ice occurs in September and October of approximately  $20 \times 10^6$  km<sup>2</sup>, with a minimum cover in February of approximately  $3 \times 10^6$  km<sup>2</sup> (Gordon, 1981). Therefore, an area amounting to  $17 \times 10^6$  km<sup>2</sup> of sea ice, which pulsates every year, would be larger than the Antarctica. Such an extension is within the seasonal ice cover, although the variations where the continent extends farther north are smaller. The seasonal variation, like the annual variation, seems to be least towards the Indian Ocean side, where the continent extends relatively far north (Deacon, 1982).

When ice is formed on the sea, the salinity of the underlying waters increases due to the diffusion of salts downwards. With the melting of the ice, the surface salinity decreases and a considerable amount of trace elements is added to the water increasing its fertility. The formation of thermohaline conditions of about 17 m in thickness has been observed at the edge of the ice shelf due to the effect of basal melting (Jacobs *et al.*, 1981). Such a freezing at the surface leading to resultant increase in the salinity is one of the mechanisms for the formation of Antarctic Bottom Water (Mosby, 1935; Deacon, 1937).

During the growth period of the ice, winds at the surface very often induce a divergence. Because of this, the sea ice also diverges leading to open water "polynya" or leads (Gordon and Taylor, 1975). The

<sup>1</sup> National Institute of Oceanography, Dona Paula, Goa-403 004.

<sup>2</sup> Department of Ocean Development, South Block, New Delhi-110 001.

most remarkable feature is the occurrence of an irregular area some 1400 km long and 400 km wide close to the Antarctic divergence between 10°E and 25°W (Gordon, 1978). Foster (1972) is of the opinion that large semi-permanent polynyas may exist near the Antarctic continent, in particular, in those regions where the coastline trends NE-SW:

The lakes in Antarctica vary from brackish to freshwater in nature, depending upon their distance from the coast. All these lakes are surrounded by bare rock outcrops. They get frozen during winter. In summer, with uninterrupted daylight warming at the surface takes place in these lakes resulting in blooms of the algae and as a result of the evaporation of the surface water some leaching of minerals occurs from the surrounding rocks. These features seem to influence the hydrochemistry of the lakes quite significantly though the cyclic changes are short-lived.

Antarctica is an uncontaminated datum point for environmental studies. Therefore, an examination of the potential pollutants should give rise to a base value for comparing with time their increase in the marine environment. In this respect, the glacial ice of Antarctica when compared with the Himalayan glaciers can indicate the concentrations of pollutants at the Southern and northern extremities of the Indian Ocean.

Utilising the unique opportunity provided by the First Indian Expedition to Antarctica, we measured several heavy metals and some major and minor ions in the Antarctic ice, in a freshwater Antarctic lake and in an adjacent polynya. We have, also, attempted a comparison of values of some of these elements with similar studies carried out earlier in a Himalayan glacier. Very few records of this type of chemical studies could be found from the available literature on Antarctica, although there are many references on record giving physical, geological and geophysical features of different regions.

### MATERIAL AND METHODS

About 10 cm of the surface ice was dug out with the help of a PVC-coated shovel and then the ice samples were collected in plastic bags. For collecting the ice samples from deeper layers, a 5 metre long, hand operated stainless steel corer was used. An acid-cleaned plastic bucket was used to collect the water samples from the lake surface. This water was preserved in a similarly cleaned PVC jerry can adjusting the pH to 3-4. Another portion of the water sample was preserved in plastic bottles. Hydrographic casts in the polynya were taken using Niskin bottles to obtain the desired volume of water and these samples were also preserved like the water samples from the lake.

All the ice samples were thawed on board the ship. A part of the melted water was used to analyse its salt content and the essential nutrients. The remaining sample was preserved in stoppered PVC bottles for further analysis in the shore laboratory.

Positions of the sampling points were, the base camp (69°59'12.7''S; 11°55'08''E); the ice shelf along the land mass (50 nautical miles south of the base camp); the *Dakshin Gangotri* lake (70°45'13''S; 11°38'14''E) and the polynya (69°58.14'S; 11°54.65'E).

On an earlier occasion snow samples from the glaciers in the Kashmir Himalayas were collected at heights varying from 2880-4100 m. In all the samples, phosphate-phosphorus, nitrate-nitrogen, nitrite-nitrogen, and silicate-silicon were analysed using the standard methods outlined by Grasshoff (1976). Methods applied were: for fluoride of Greenhalgh and Riley (1961); bromide of Saenger (1972); calcium and magnesium of Culkin and Cox (1966); heavy metals of Brewer *et al* (1969). Iodide was analysed by an ion-selective electrode and potassium by atomic absorption spectrophotometry. Analytical instruments used were a UV-Vis spectrophotometer (Spectronic 710B), an atomic absorption spectrophotometer (Hilger-Watts H-1550) and an ion analyzer (Orion).

## RESULTS AND DISCUSSION

(i) **Ice:** It is known that the sea water ice first accumulates a large amount of nutrients (Sen Gupta, 1973) but as the ice freezes, the salts are lost into the water below. With the growth of the ice, the salts diffuse further down. Thus, a vertical gradient occurs showing increasing values downwards and the lowest at the surface. Almost all the constituents shown in Table 1 gave an increasing trend downwards. Most of the elements present in the ice can be expected to be fully of seawater origin, perhaps, except fluoride and bromide. These two halides decrease with depth in the ice. Some distance away from the coast there was no significant difference in the concentration of almost all constituents. This probably indicates that the ice at the base camp and at the shelf are of similar origin. Fluoride and bromide at the surface of the shelf edge and at 1 m depth of the base camp appear to be influenced mostly by the atmospheric transport of aerosols which probably diffuse downwards. Higher chloride values at the shelf also appear to be as a result of their transport from the atmosphere. The presence of nitrite in the samples with small concentrations of nitrate would indicate the possibility of reduction in the latter, as the air bubbles, trapped inside the ice, escape very rapidly. A reducing environment is, thus, created in the ice. Productivity at the surface of the ice shelf was  $0.22 \text{ mg C m}^{-3} \text{ day}^{-1}$  and the total bacterial count was  $63 \text{ g}^{-1}$  of ice (Matondkar, 1982a).

TABLE 1

*Concentrations of nutrients and a few major elements in ice and water at Princess Astrid Coast, Antarctica.*

| Station                     | Phosphate<br>$\mu\text{g-at/l}$ | Nitrite<br>$\mu\text{g-at/l}$ | Nitrate<br>$\mu\text{g-at/l}$ | Silicate<br>$\mu\text{g-at/l}$ | Fluoride<br>$\text{mg/l}$ | Bromide<br>$\text{mg/l}$ | Iodide<br>$\mu\text{g/l}$ | Calcium<br>$\text{mg/l}$ | Magnesium<br>$\text{mg/l}$ | Potassium<br>$\text{mg/l}$ | Chloride<br>$\mu\text{g/l}$ |
|-----------------------------|---------------------------------|-------------------------------|-------------------------------|--------------------------------|---------------------------|--------------------------|---------------------------|--------------------------|----------------------------|----------------------------|-----------------------------|
| Base Camp 1m                | 0.78                            | 0.49                          | 0.25                          | 0.51                           | 0.08                      | 0.35                     | 0                         | 2.1                      | 6.9                        | 3.7                        | —                           |
| 3 m                         | 0.51                            | 0.24                          | 0.40                          | 0.36                           | 0.08                      | 0                        | 0                         | 0.5                      | 2.4                        | 1.0                        | 0.001                       |
| 4 m                         | 0.59                            | 0.26                          | 0.36                          | 0.39                           | 0.03                      | 0                        | 0                         | 1.3                      | 4.0                        | 2.0                        | 0.002                       |
| 5 m                         | 0.65                            | 0.45                          | 1.10                          | 0.42                           | 0.03                      | 0                        | 0                         | 2.1                      | 6.6                        | 3.1                        | —                           |
| Ice Shelf-Land<br>Mass edge | 0.84                            | 0.26                          | 1.15                          | 0.33                           | 0.10                      | 0.68                     | 0                         | 1.6                      | 5.0                        | 3.2                        | 0.002                       |
| Antarctic Lake              | 0.64                            | 0.56                          | 2.04                          | 26.97                          | 0.51                      | 0.69                     | 0                         | 107.0                    | 67.1                       | 54.3                       | 0.013                       |
| Polynya-surface             | 1.47                            | 0.68                          | 8.71                          | 106.85                         | 1.30                      | 0.67                     | 8                         | 409                      | 1266                       | —                          | 18.89%                      |

(ii) **Lake:** The freshwater antarctic lake was surrounded by exposed rocks and probably gets frozen during the winter. In a closed basin such as this the inorganic composition seems to be dependent not only on the materials coming from different sources which get dissolved in the water, but also from those which get down to the water after evaporation. The sources of addition to this lake appear to be the melted water from the surrounding glacier. As the observations were taken during the summer, evaporation will also be playing a significant role in regulating the concentrations of the elements in the lake.

Lakes in the colder countries of the northern hemisphere have been reported (Hutchinson, 1957) to contain on an average  $10.8\text{--}38.3 \mu\text{g/l PO}_4^{3-}\text{-P}$ ;  $32\text{--}90 \mu\text{g/l NO}_3^-\text{-N}$ ;  $1.11\text{--}48.1 \mu\text{g/l SiO}_4^{4-}\text{-Si}$ ;  $0.25 \text{ mg/l K}^+$ ;  $0.13 \text{ mg/l Ca}^{2+}$ ;  $0.1\text{--}0.5 \text{ mg/l F}^-$  and  $4.5 \text{ mg/l Br}^-$ .

The values given in Table I for  $\text{PO}_4^{3-}\text{-P}$   $20 \mu\text{g/l}$ ;  $\text{NO}_3^-\text{-N}$   $28.6 \mu\text{g/l}$ ;  $\text{NO}_2^-\text{-N}$   $7.8 \mu\text{g/l}$ ;  $\text{F}$   $0.51 \text{ mg/l}$  for this Antarctic lake are quite comparable with those of the Arctic lake.

However, significantly high values were recorded for  $\text{SiO}_4^{4-}\text{-Si}$   $756 \mu\text{g/l}$ ;  $\text{K}^+$   $54.3 \text{ mg/l}$ ;  $\text{Ca}^{2+}$   $107 \text{ mg/l}$ ;  $\text{Mg}^{2+}$   $67.1 \text{ mg/l}$ ; and a very low value of  $0.69 \text{ mg/l}$  for  $\text{Br}$ .

Igneous and sedimentary rocks have been observed to contain  $9.8$  and  $8.0 \text{ mg/l K}^+$ ,  $33.1$  and  $34.0 \text{ mg/l Mg}^{2+}$ ,  $37.1$  and  $53.2 \text{ mg/l Ca}^{2+}$  respectively (Hutchinson, 1957). The high values of these in the lake water cannot be only due to weathering and leaching from metamorphic rocks present all around the lake. These processes can be expected to proceed very slowly due to low temperature. It appears that the melted water from the glaciers should contain significant amounts of these elements. The summer evaporation also plays an important role in increasing the concentration.

Concentrations of nutrients in the lake help in stimulating the rate of phytoplankton production during the summer. Photosynthetic productivity of  $0.38 \text{ mg C.m}^{-3} \text{ day}^{-1}$  and bacterial count of  $24 \times 10^4/\text{ml}$  have been recorded from the lake (Matondkar, 1982b).

(iii) **Heavy Metals:** As has been noted earlier, Antarctica is an uncontaminated datum point for environmental studies. Some of the heavy metals examined are considered as potential pollutants. Therefore, these have been treated here separately. The concentrations of these metals at the surface of the Antarctic lake is because of the influence of melting ice coming from the glacier. We have, therefore, attempted a comparison of the lake values with the values obtained from snow samples, collected at varying heights from a Himalayan glacier.

Table 2 gives the values for the metals. Antarctic ice shelf is of marine origin. The similarity of values for most of the metals between the Antarctic ice and the polynya (10 m) confirms this. Higher values for zinc and the presence of cobalt, lead and cadmium in the surface waters (10 m) of the polynya and their absence in the ice is most probably as a result of downward diffusion of salt in the ice column. The surface of the ice is very much influenced by the atmospheric transport of aerosols caused by katabatic wind. The presence of manganese in the ice and the absence of the same in the polynya should be due to such an effect.

TABLE 2  
*Concentrations of a few heavy metals (in  $\mu\text{g/l}$ ) in ice and water, Princess Astrid Coast, Antarctica and in a glacier in the Kashmir Himalayas.*

| Station                  | Fe   | Zn   | Cu  | Mn   | Ni  | Co  | Pb  | Cd  |
|--------------------------|------|------|-----|------|-----|-----|-----|-----|
| Antarctic Ice            | 1.4  | 14.4 | 3.0 | 6.8  | 2.0 | 0   | 0   | 0   |
| Antarctic Lake           | 50.5 | 13.6 | 3.4 | 5.6  | 3.2 | 0   | 0   | 0   |
| Polynya - 10 m           | 2.0  | 46.8 | 3.1 | 0    | 3.7 | 1.4 | 2.6 | 1.5 |
| Himalayan Glacier (mean) | 82.5 | 4.5  | 4.1 | 17.0 | 1.8 | 1.1 | 3.1 | 0   |

Surface water of the lakes in the colder countries of the northern hemisphere hold on an average  $90\text{-}160\mu\text{g/l}$  Fe;  $33\text{-}44\mu\text{g/l}$  Mn;  $9\text{-}210 \mu\text{g/l}$  Cu;  $5.6\text{-}18 \mu\text{g/l}$  Zn;  $5\text{-}20 \mu\text{g/l}$  Ni;  $2.3\text{-}6.7 \mu\text{g/l}$  Co; and  $26 \mu\text{g/l}$  Pb in them (Hutchinson, 1957). Occasionally enormously high concentrations of Fe are recorded in some of them, which may be due to the atmospheric transport of pollutants.

Values for all the metals in the surface waters of the Antarctic lake were significantly lower than all the ranges mentioned above, while Co, Pb and Cd were absent. This clearly indicates the uncontaminated nature of the environment. The closeness of some of these values with the mean values for the same elements observed in the Himalayan glacier testifies to the similarities in the chemical characteristics of these two environments.

Table 3 gives the altitudewise variation of the metals in the Himalayan glacier. There is not much change from 2880 m to 4100 m which signifies that probably the source of these metals is the air mass and with time not much change has occurred in their concentrations.

TABLE 3  
*Concentrations of a few heavy metals (in  $\mu\text{g/l}$ ) at varying heights on a glacier in the Kashmir Himalayas*

| Place & height | Fe   | Zn  | Cu  | Mn   | Ni  | Co  | Pb  | Cd |
|----------------|------|-----|-----|------|-----|-----|-----|----|
| Baltal 2880 m  | 80.6 | 4.1 | 3.7 | 11.8 | 1.7 | 0   | 4   | 0  |
| Sangam 3569 m  | —    | 4.4 | 5   | —    | 6.6 | 3.3 | 5.2 | 0  |
| Neh Nar 4100 m | 78.3 | 5   | 3.7 | 28.7 | 1.8 | 0   | 0   | 0  |

## Chemical Studies on the Ice...

This is the first time such data have been collected from two clean environments at the two extremities of the Indian Ocean. Application of these as a reference or datum point will help to delineate the changes in the degree of contamination in the Indian Ocean.

(iv) **Polynya** The depth in the polynya varied from 203 m at the edge of the ice shelf to 210 m at the extreme end bordered by sea ice. The hydrographical and hydrochemical data, collected from the polynya, have been presented in Tables 4 A & B. A diurnal observation of plankton indicated a dense bloom of phytoplankton dominated by *Fragilaria* and *Rhizosolenia* Spp. (J. Goes - personal communication). Measurements of photosynthetic productivity gave a value of  $0.97 \text{ mg C.m}^{-3} \text{ day}^{-1}$  while the total bacterial count was  $3.8 \times 10^4 \text{ ml}^{-1}$  (Matondkar 1982a).

TABLE 4  
*Hydrochemical Components in the Polynya at Princes Astrid Coast, Antarctica*  
A: Temperature, Salinity, Dissolved Oxygen, Nutrients and a few Major and Minor Elements

| Depth (m) | T°C   | ‰     | O <sub>2</sub><br>ml/l | PO <sub>4</sub> | NO <sub>2</sub> | NO <sub>3</sub> | Si    | Ca        | Mg   | K | F    | Br | I  |
|-----------|-------|-------|------------------------|-----------------|-----------------|-----------------|-------|-----------|------|---|------|----|----|
|           |       |       |                        | (in µg-at/l)    |                 |                 |       | (in mg/l) |      |   |      |    |    |
| 0         | -1.36 | 34.12 | 7.63                   | 1.47            | 8.71            | 0.68            | 106.8 | 409       | 1266 | — | 1.31 | 67 | 8  |
| 50        | -1.69 | 34.25 | 7.21                   | 1.45            | 9.56            | 0               | 107.0 | 413       | 1266 | — | —    | —  | —  |
| 100       |       |       | 7.83                   | 1.27            | 9.34            | 0               | 108.1 | 416       | 1260 | — | 1.30 | 69 | 12 |
| 150       | -1.85 | 34.25 | 4.63                   | 0.90            | 4.49            | 0.93            | 108.3 | 412       | 1275 | — | 1.31 | 68 | 10 |

B: Heavy Metals Dissolved (D) in µg/l and Particulate (P) in µg/g wet weight

| Depth | Fe |      | Zn   |      | Cu  |      | Mn  |      | Ni  |      | Co  |    | Pb  |    | Cd  |     |
|-------|----|------|------|------|-----|------|-----|------|-----|------|-----|----|-----|----|-----|-----|
|       | D  | P    | D    | P    | D   | P    | D   | P    | D   | P    | D   | P  | D   | P  | D   | P   |
| 10 m  | 2  | 632  | 46.8 | 87.5 | 3.1 | 26.7 | 0   | 33.2 | 3.7 | 175  | 1.4 | ND | 2.6 | 13 | 1.5 | 5.2 |
| 200 m | 4  | 55.5 | 12   | 23.2 | 3   | 3.2  | 2.7 | ND   | 3.5 | 20.2 | 1.4 | ND | 1.7 | ND | 0.5 | 5.7 |

ND = not detectable

Table 4 A indicates a haline convection at the surface layers, which is usual in the polynyas and leads of Antarctica, (Foster, 1972; Dera, 1980). Due to basal melting of the ice, a thin layer of lower salinity can be expected at the surface. The temperature decreased with depth, progressively.

An examination of the nutrient-data given in Table IV A indicates low values for dissolved oxygen, phosphate-phosphorus and nitrate-nitrogen. The presence of nitrite-nitrogen at 150 m depth was also recorded. This indicates a watermass distinctly separate from the overlying water. This is probably the water mass which can be expected to glide over the shelf of the Antarctica and may form a part of the deeper water masses in the Southern Ocean. However, we are not postulating any new source of the Antarctic Deep Water. It is probably the same water with a new characteristic. The character of this water can also be identified from the differences in the concentrations of conservative and semi-conservative major ions such as calcium, magnesium, fluoride and bromide as compared to those in the overlying water mass (Table 4 A).

Table 4 B indicates the difference in the concentrations of heavy metals in the surface and deep water layers of the polynya. Basal melting of the ice adds a large quantity of dissolved and specially the particulate material to the waters around. Large differences in the concentrations of the particulate fractions of the heavy metals between the two sampling depths confirm this. The water at 10 m depth was heavily influenced by the melted ice, while the deeper water had all the characteristics of the ocean.

From a comparison of the chemical components given in Tables 4 A and B, it can be inferred that the base of the ice shelf, surrounding the polynya, should be between 100 and 150 m, while its height above the sea level was about 20 m. In any case, the land mass covered with ice would be some distance inside from the area of our observation.

Nutrients at the surface were fairly high. The rate of photosynthetic production was also quite high. A phytoplankton bloom was seen in progress at the time of observation. Nutrients at the surface combined with those added by the melting of ice created an enormous pool of nutrient reserve which promoted high production rates influenced by the continuous daylight during the prolonged summer. It, however, cannot use the nutrient reserve. This is one of the reasons for the high nutrient values and particularly for silicate-silicon which recorded very high values at the depths of the Indian Ocean.

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