

## **Dissolved Carbonate-Carbon Dioxide in Sea Water of the South China Sea, Area II: Sabah, Sarawak and Brunei Darussalam**

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### **Abstract**

Dissolved carbonate species in seawater are determined from pH and total alkalinity. The data clearly pointed out the significance of Rajang River as a source of organic matters that were subsequently decomposed and cause CO<sub>2</sub> gas to evade from nearshore water in its vicinity into the atmosphere while most offshore surface water was the sink of atmospheric CO<sub>2</sub>. The total alkalinity profiles indicated dissolution of carbonate minerals, believed to be high magnesian calcite, below 500 m, which reinforce CO<sub>2</sub> storing capacity of these waters.

### **Introduction**

Dissolved inorganic carbon (DIC) comprises of carbon dioxide gas (CO<sub>2</sub>), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonation (HCO<sub>3</sub><sup>-</sup>) and carbonation (CO<sub>3</sub><sup>2-</sup>). The total concentration of DIC and ratios among all species are influenced by several factors, particularly partial pressure of CO<sub>2</sub>, total and carbonate alkalinity, and physical factors such as temperature, salinity and pressure. The net effect on speciation of the species results in the observed pH of seawater.

Photosynthesis consumes CO<sub>2</sub> gas and thus decreases partial pressure of CO<sub>2</sub> while respiration and decomposition of organic matter do the opposite. Dissolution of carbonate mineral uses up CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup> and lowers total alkalinity while calcification does the opposite. By understanding the carbonate system in seawater, these processes can be explained.

### **Methods**

Seawater was collected at each station during Cruise 34 (10 July – 2 August 1996) and 41 (1-24 May 1997) at selected depths by water sampler attached to a rosette system. The methods for pH and total alkalinity determination and calculation for dissolved carbonate species were given in Rojana-anawat and Snidvongs (1997).

To compare the horizontal concentration of each species so that non-conservative processes could be seen, the concentrations on isopycnal surfaces, i.e. the surface that frictionless water can flow without any energy loss or gain; four isopycnal surfaces were chosen at sigma theta (density anomaly) of 23.0, 25.0, 27.0 and 27.5 kg m<sup>-3</sup> plus sea surface.

### **Results**

#### Vertical Distribution

In this area, pH of seawater decreased from about 8.2 at the surface is 7.7 at about 500 m. Between 500 and 2000 m, pH changed only slightly (Figure 1). This type of pH profile for both cruises implied strong biological activities, photosynthesis and respiration, between subsurface and 500 m.

The total alkalinity increased quite rapidly from about 2.2 meq l<sup>-1</sup> at the surface to about 2.35 at 150 m. Below 150 m, total alkalinity gradually increased, although the increasing rate was smaller

than in the subsurface zone (Figure 2). This evidence suggested that different processes controlled pH and total alkalinity of seawater in this area though these processes could be well interrelated. Dissolution of carbonate mineral was likely to be the cause of alkalinity increasing in deep water.

The total concentration of dissolved inorganic carbon in seawater increased from less than 2 mM at sea surface to more than 2.3 mM at 2000 m (Figure 3), due mainly to respiration in the water column. Dissolved bicarbonate ( $\text{HCO}_3^-$ ) accounted for 88 - 97 % of the total dissolved inorganic carbon.

The concentration of dissolved carbonate, although a minor specie of dissolved inorganic carbon, determined the stability of different carbonate minerals exposed to the water. Despite the fact that all water samples collected from this area were supersaturated with respect to pure calcite and aragonite minerals, seawater below 500 m was undersaturated with respect to high magnesian calcite (Figure 4). Dissolution of these calcite minerals containing more than 5 mol% of Mg could explain the gradual increase in total alkalinity with depth.

Partial pressure of dissolved carbon dioxide gas in surface seawater of the study area was generally near equilibrium with the present day atmospheric partial pressure of 360 matm. The partial pressure below 1000 m was around 1400 matm with the range of 1200 - 1600 matm (Figure 5).

### Horizontal Distributions

Isopycnal surface was usually more depressed offshore and to the east of Sabah (Figures 11A-D). However, deep water pycnocline depression below 1000 m was found along longitude 112°E (Figure 11E). Intermediate water ( $q_t = 23 - 25 \text{ kg m}^3$ ) was found between 50 - 140 m while deep water ( $q_t > 27 \text{ kg m}^3$ ) was found below 600 m.

pH of surface water was low nearshore especially near Kuching (Figure 6A) suggesting the decay of terrestrial organic matters delivered by the river. The pH of intermediate water was also generally lower off Kuching and Sabah (Figures 6B and C). There was little variation of pH of deep water (Figures 6D and E).

Freshwater discharge from Kuching area also caused total alkalinity of surface water to decrease (Figure 7A). However, this effect could be only slightly detected in intermediate water (Figures 7B and C) and deep water (Figures 7D and E). It seems quite clear that the dissolution of carbonate mineral was the main source of alkalinity than river input.

Although decomposition of organic material input by Rajang River was a major source of inorganic carbon to the surface water of Kuching area, the total dissolved inorganic carbon actually observed in surface water was low (Figure 8A). This was because the water had low alkalinity and thus less capacity to store inorganic carbon as negative charge ions, such as  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . Dissolved inorganic carbon in intermediate water (Figures 8B and C) was less subjected to input/output and the concentration was quite homogeneous horizontally. Deep water had high concentration of dissolved inorganic carbon due to the net respiration while high pressure and low temperature favored more  $\text{CO}_2$  to be dissolved.

The concentration of dissolved carbonate in surface and intermediate waters which was always higher than 0.1 mM (Figures 9A - C) clearly indicated that these waters were supersaturated with respect to all major carbonate minerals. However, deep water in the study area that had carbonate concentration less than 0.1 mM could be undersaturated with respect to high magnesian calcite.

Partial pressure of dissolved carbon dioxide in surface water also pointed out that nearshore water the influence from Rajang River which had the partial pressure higher than 360 matm was the source of  $\text{CO}_2$  to the atmosphere while offshore water was generally the sink of atmospheric  $\text{CO}_2$  (Figure 10A). Partial pressure of dissolved  $\text{CO}_2$  in intermediate water reflected local processes that also highly varied with time (Figures 10B - C). However, the distribution pattern of deep water  $\text{pCO}_2$  was quite the same for both cruises, although the absolute pressure varied slightly, that might indicate a rather stable process involving  $\text{CO}_2$  in deep water layer.

## Discussion and Conclusion

The major findings in this study were that Rajang River was a major source of organic matters that subsequently decayed and caused  $\text{CO}_2$  to evade from nearshore into the atmosphere, while most offshore water was the sink of atmospheric  $\text{CO}_2$ . Dissolution of carbonate mineral, believed to be high magnesian calcite, took place below 500 m. This suggested that high magnesian calcite such as coccolith and foraminifera shells would be absent from sediment samples below 500 m. In general, this area is important as a sink for atmospheric  $\text{CO}_2$  and deserved more precise estimation of flux and processes involved.

## References

Rojana-Anuwat, P. and Sninddvongs, S. 1997 Dissolved oxygen and carbonate-carbon dioxide in sea water of the south China sea, Area I : Gulf of Thailand and the East Coast of Peninsular Malaysia, SEAFDEC Collaborative Proceeding (in press)

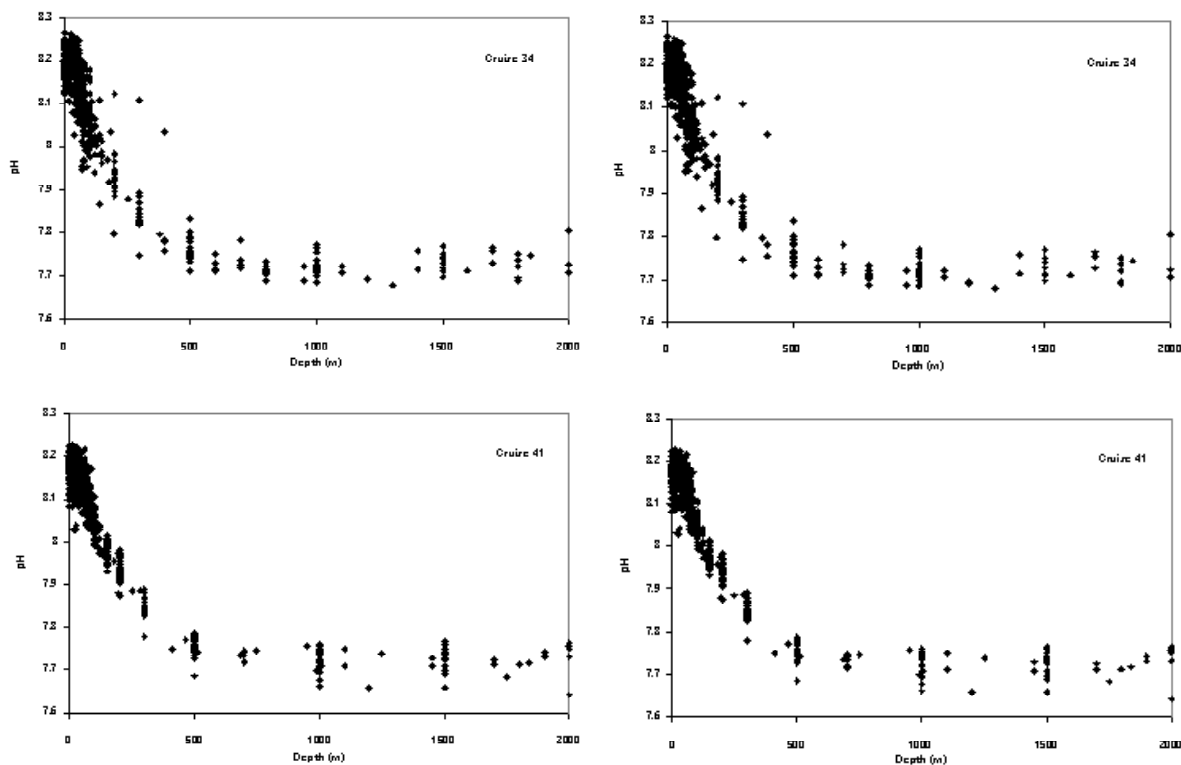


Fig. 1 Pooled vertical pH profiles for Cruises 34 and 41

Fig. 2 Pooled vertical profiles of total alkalinity for Cruises 34 and 41

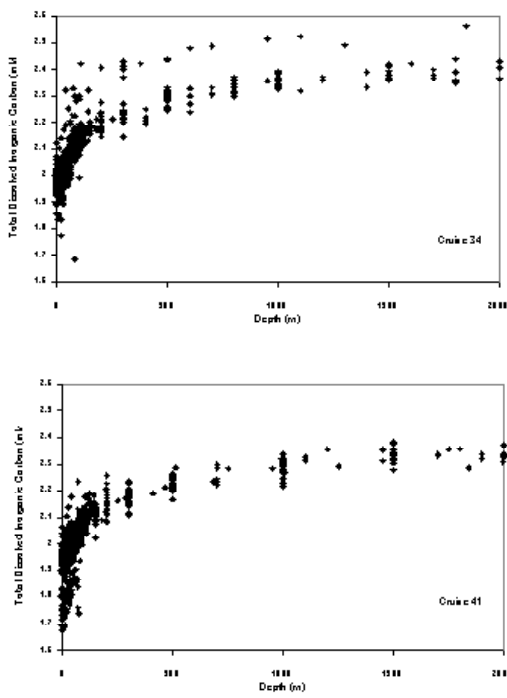


Fig. 3 Vertical profiles of total dissolved inorganic carbon for Cruises 34 and 41

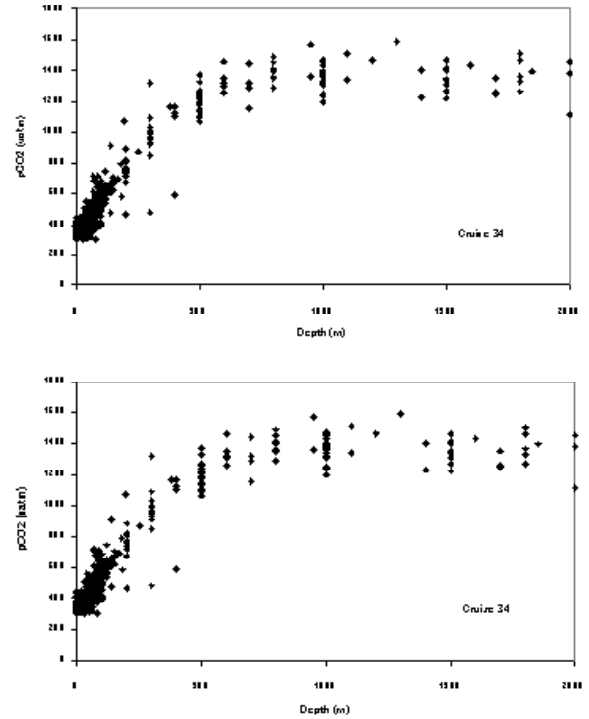


Fig. 5 Pooled vertical profiles of dissolved carbon dioxide partial pressure for Cruise 34 and 41

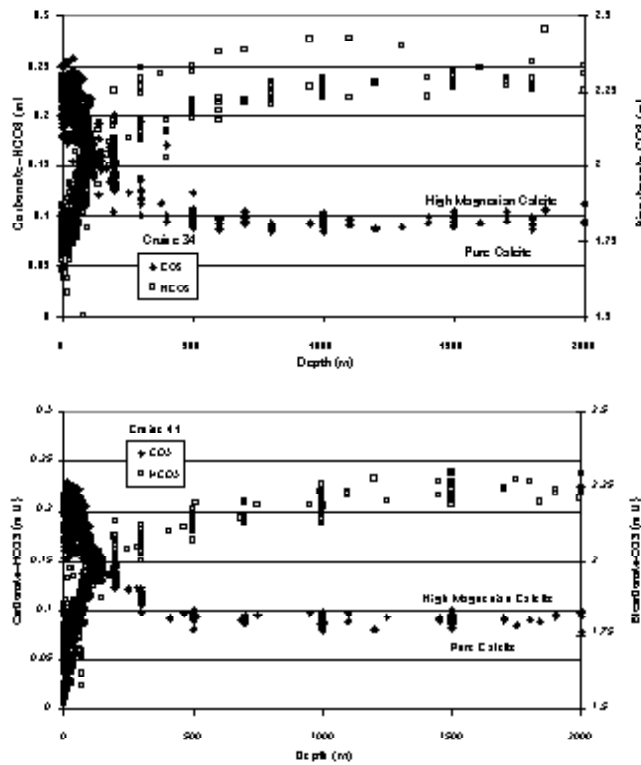


Fig. 4 Pooled vertical profiles of dissolved bicarbonate and carbonate. Equilibrium concentrations of carbonate with respect to pure calcite and “high” magnesian calcites are shown at 0.05 and 0.1 mM

S2/OG4<ANOND>

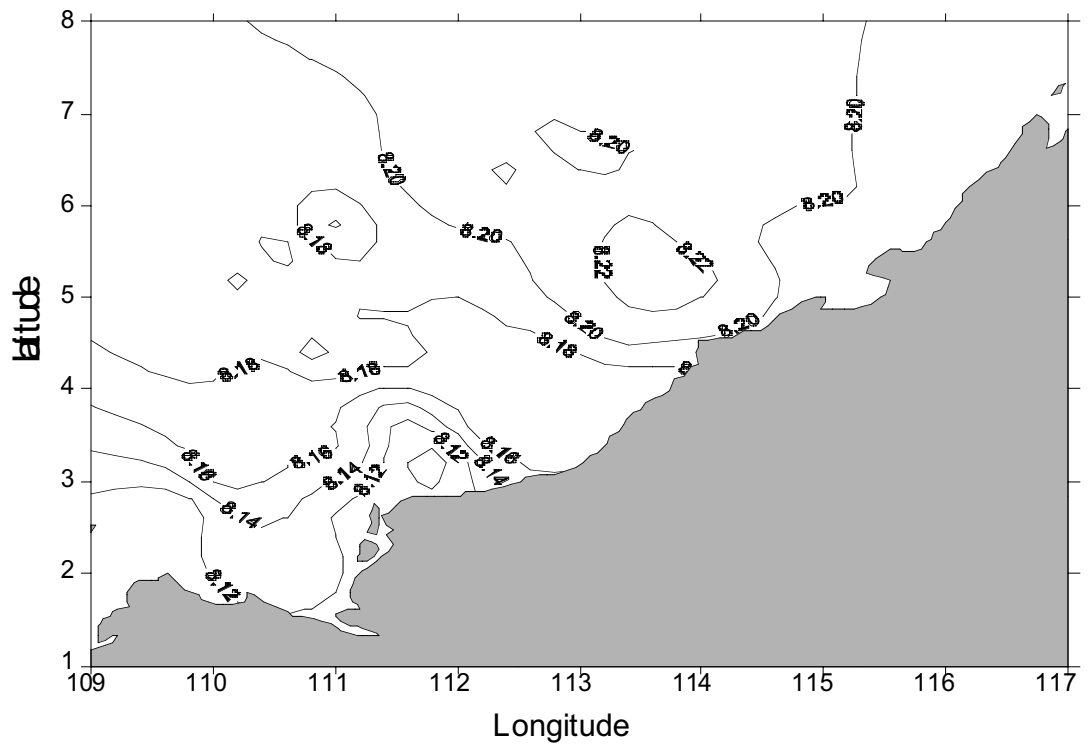
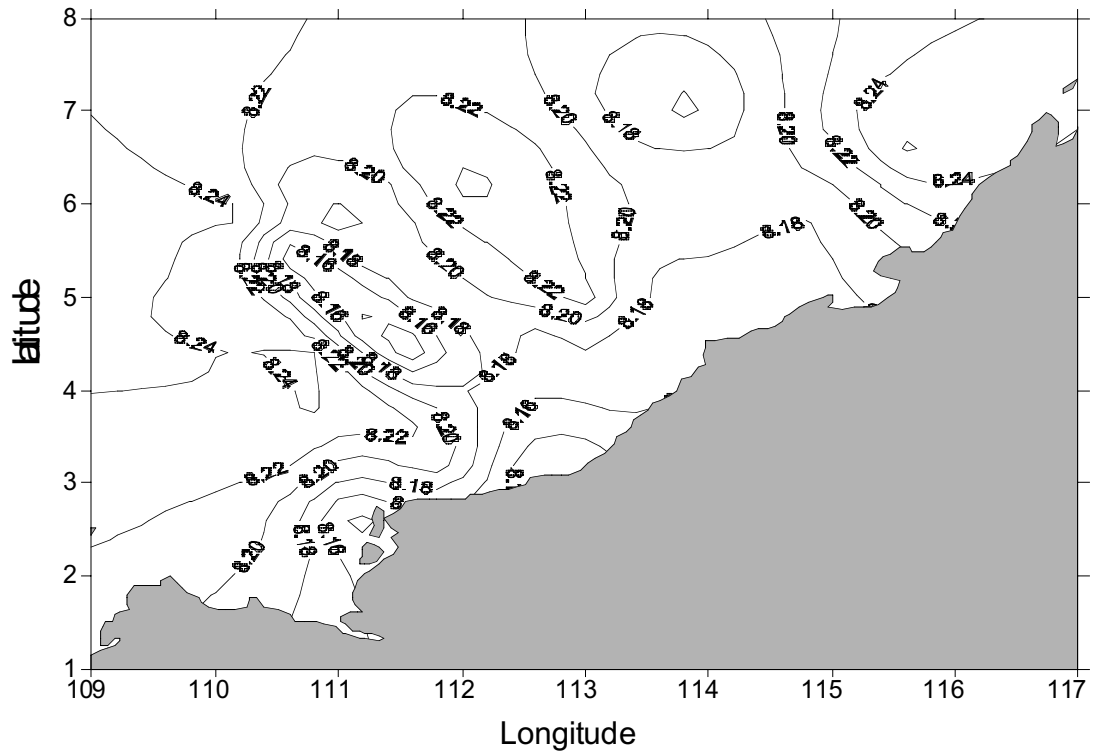


Fig. 6A pH at sea surface

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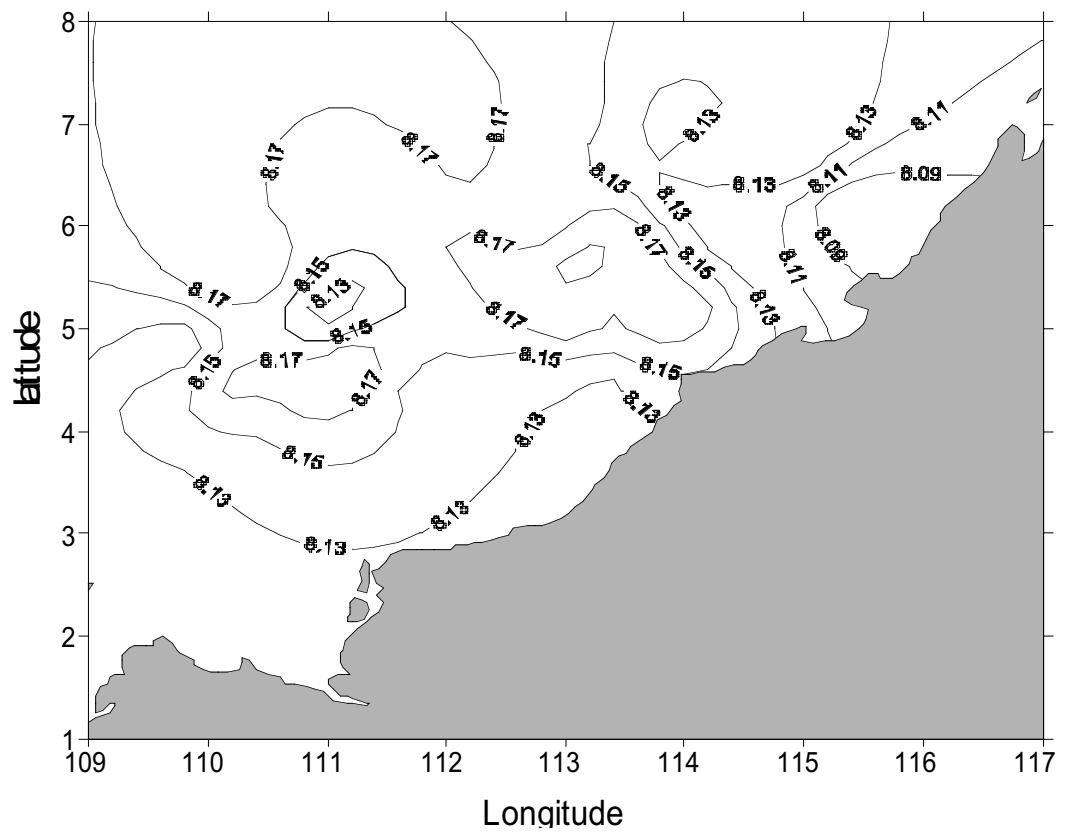
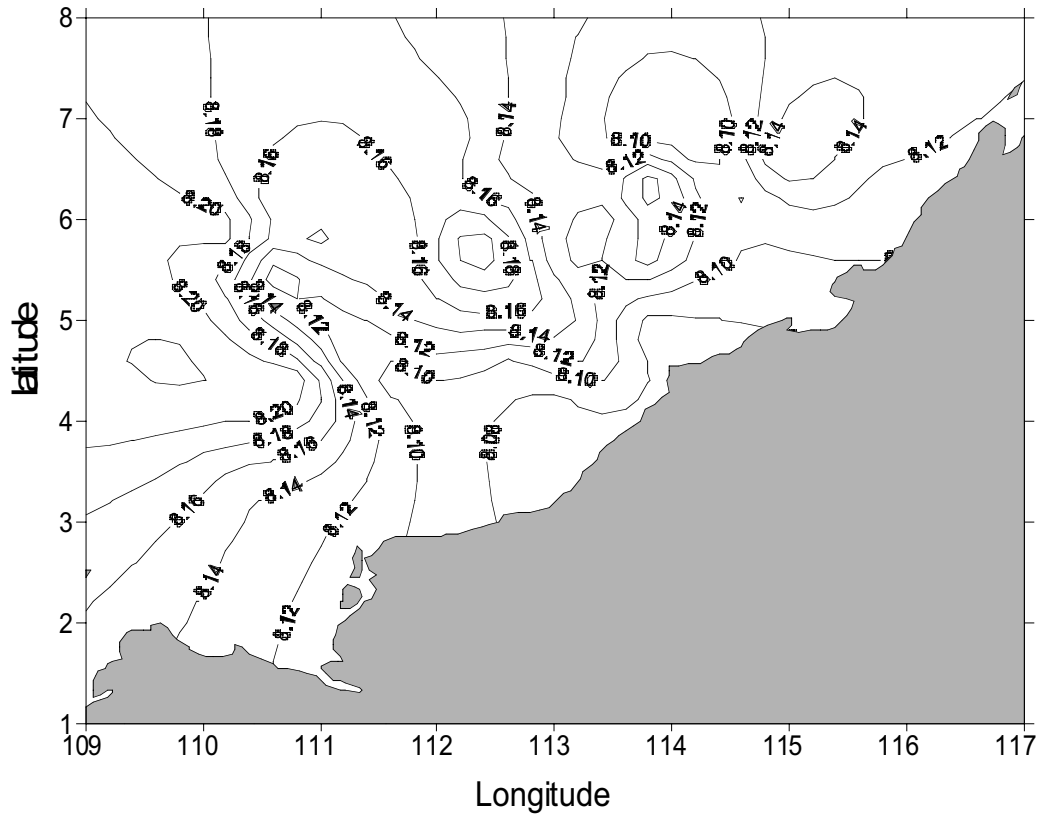


Fig. 6B pH on the 23.0 kg/m<sup>3</sup> isopycnal surface

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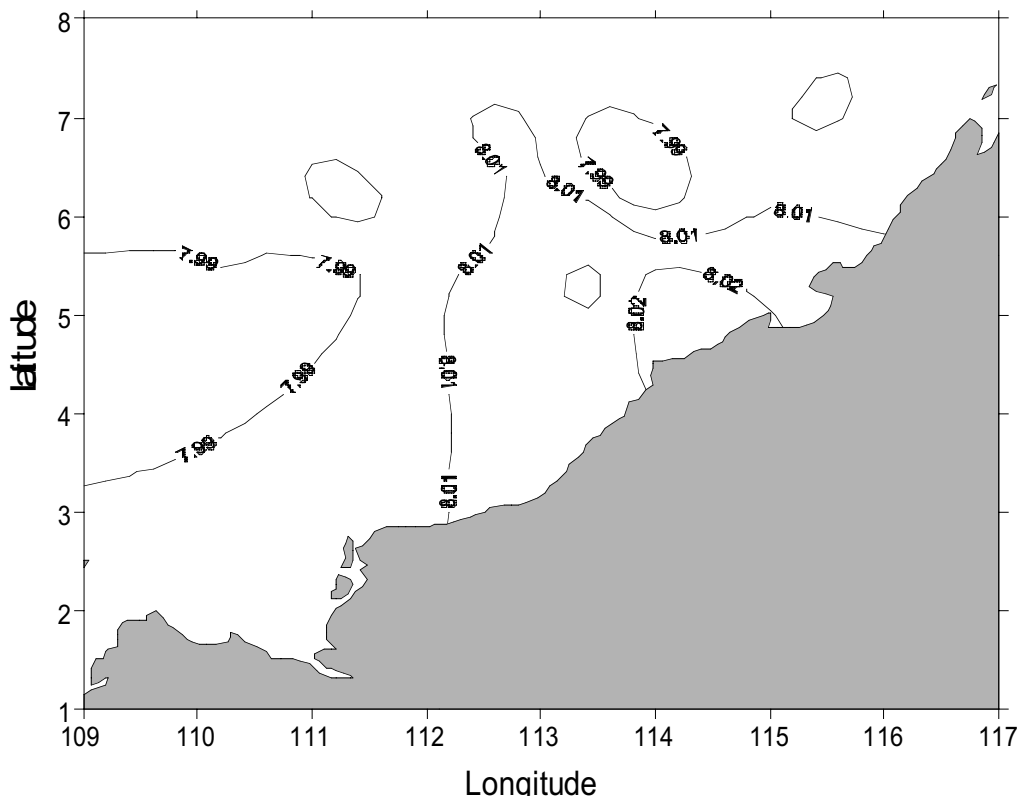
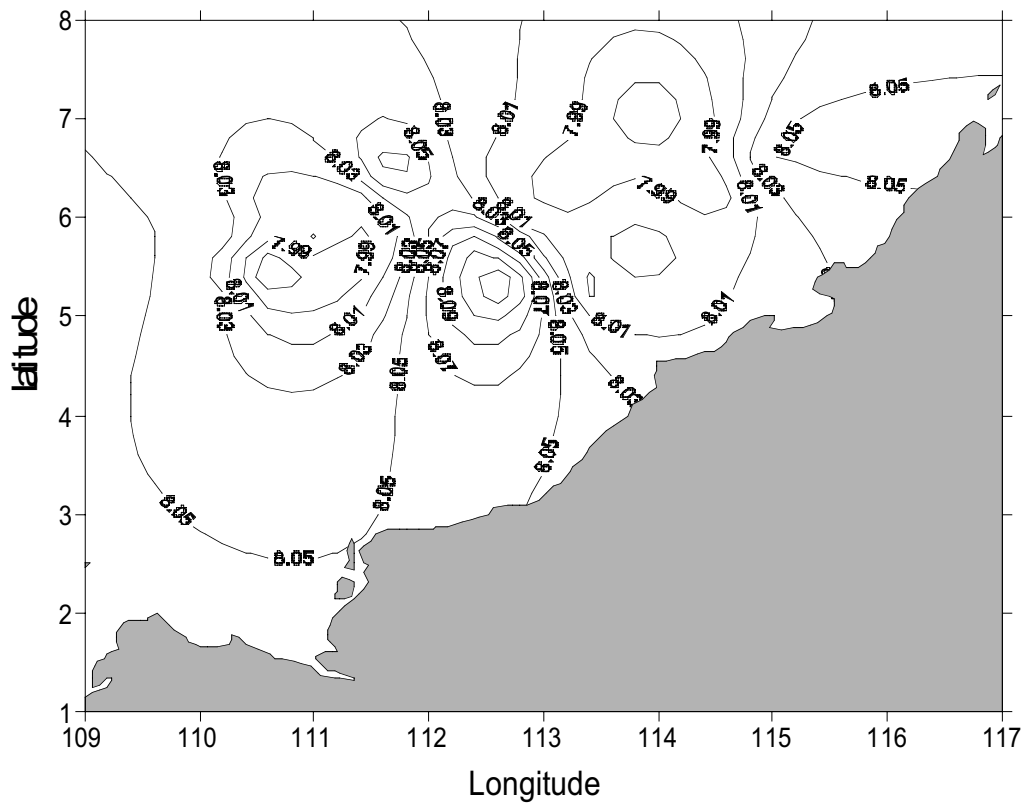


Fig. 6C pH on the 25.0 kg/m<sup>3</sup> isopycnal surface

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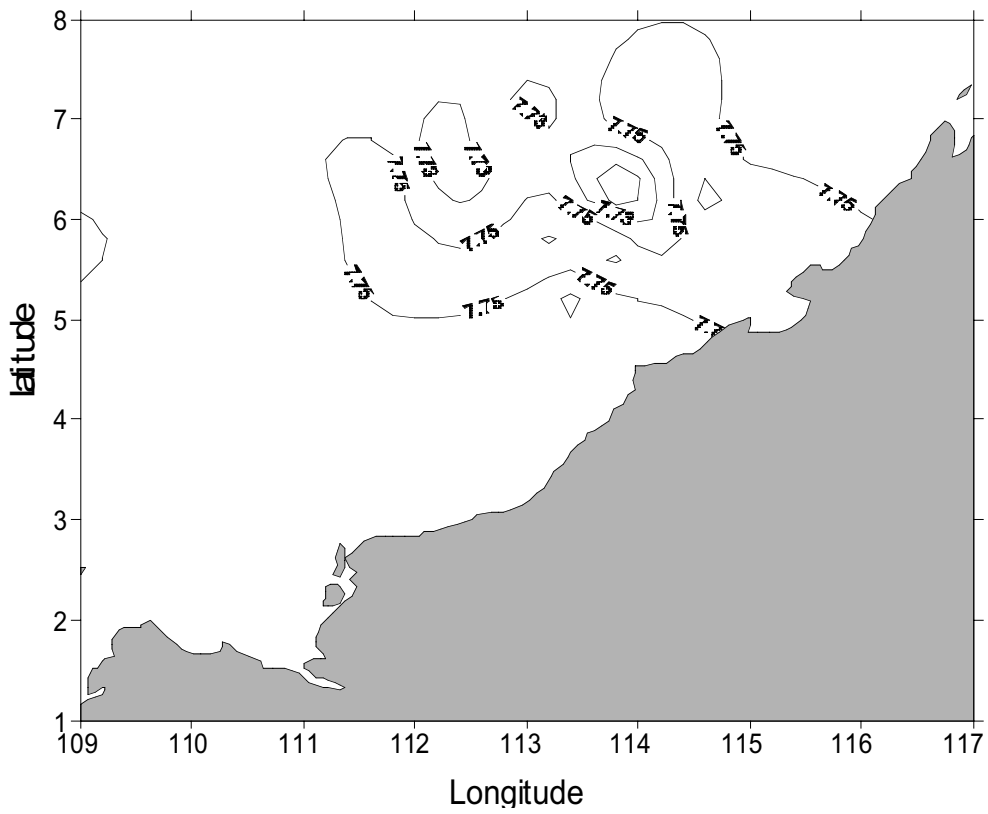
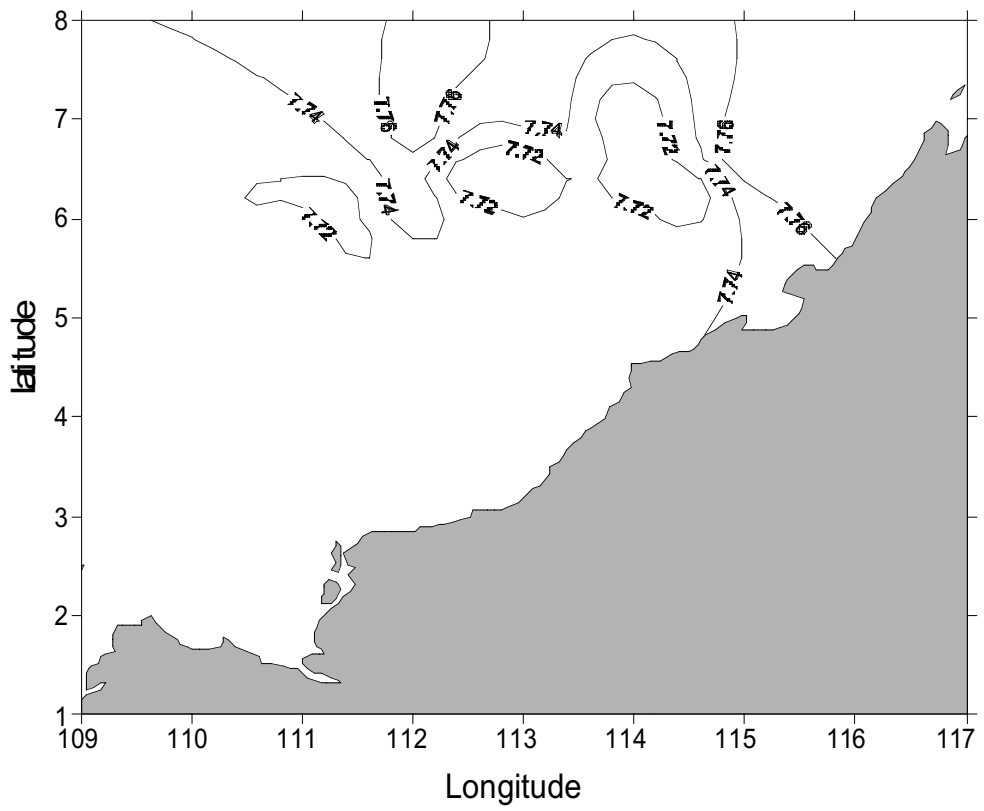


Fig. 6D pH on the 27.0 kg/m<sup>3</sup> isopycnal surface



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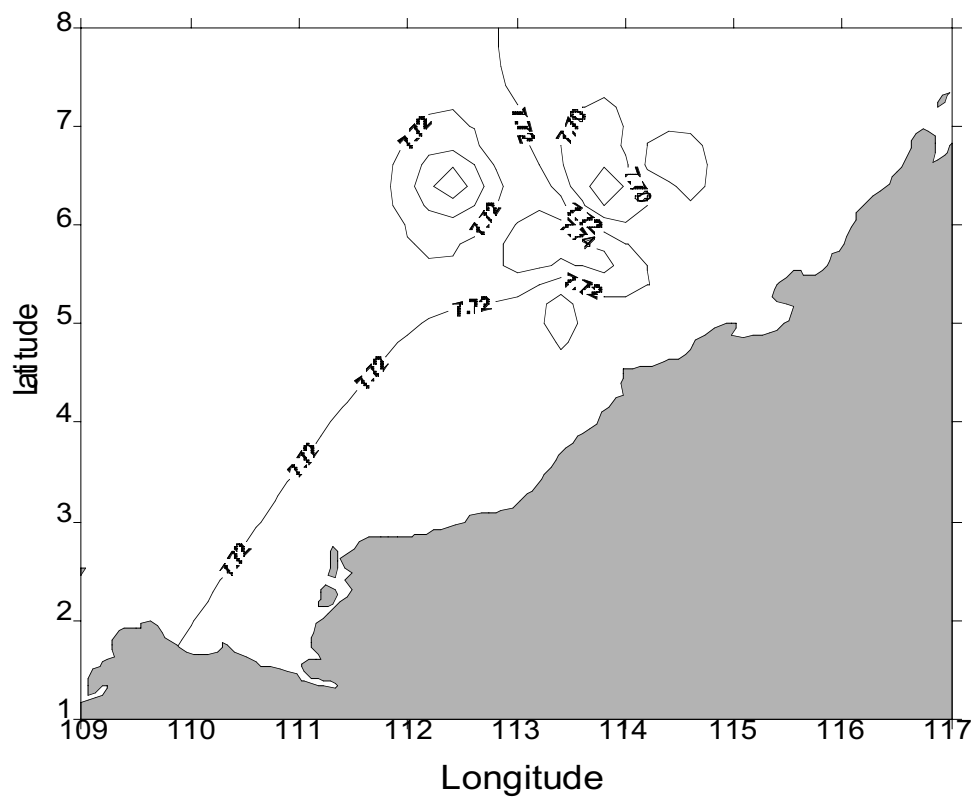
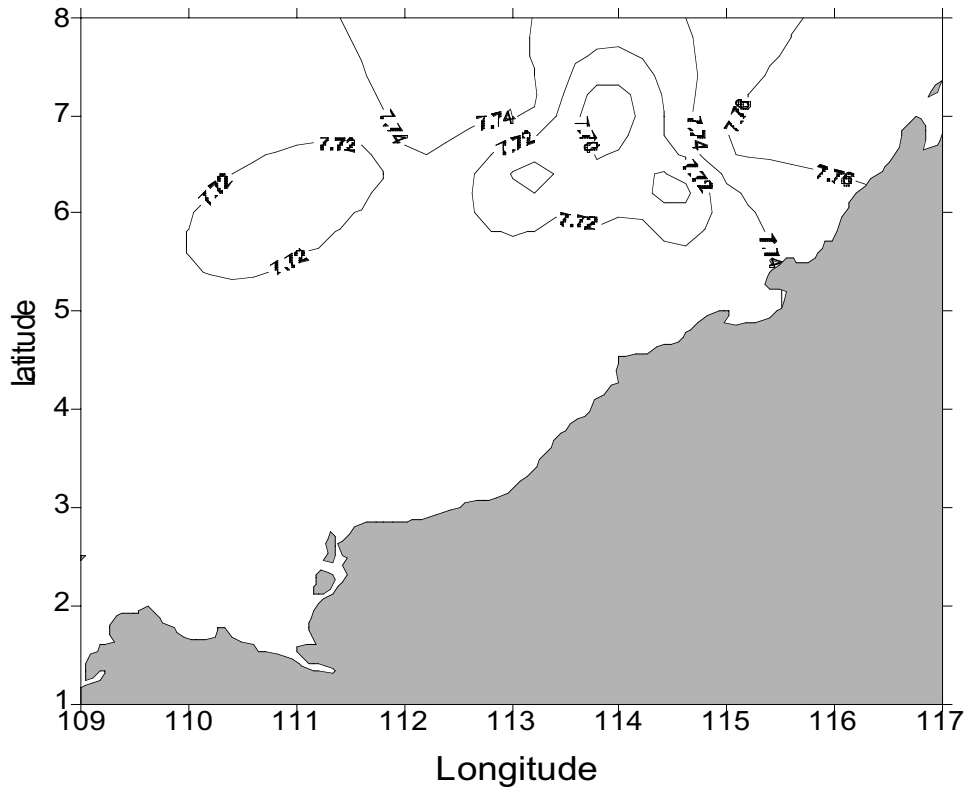


Fig. 6E pH on the 27.5 kg/m<sup>3</sup> isopycnal surface

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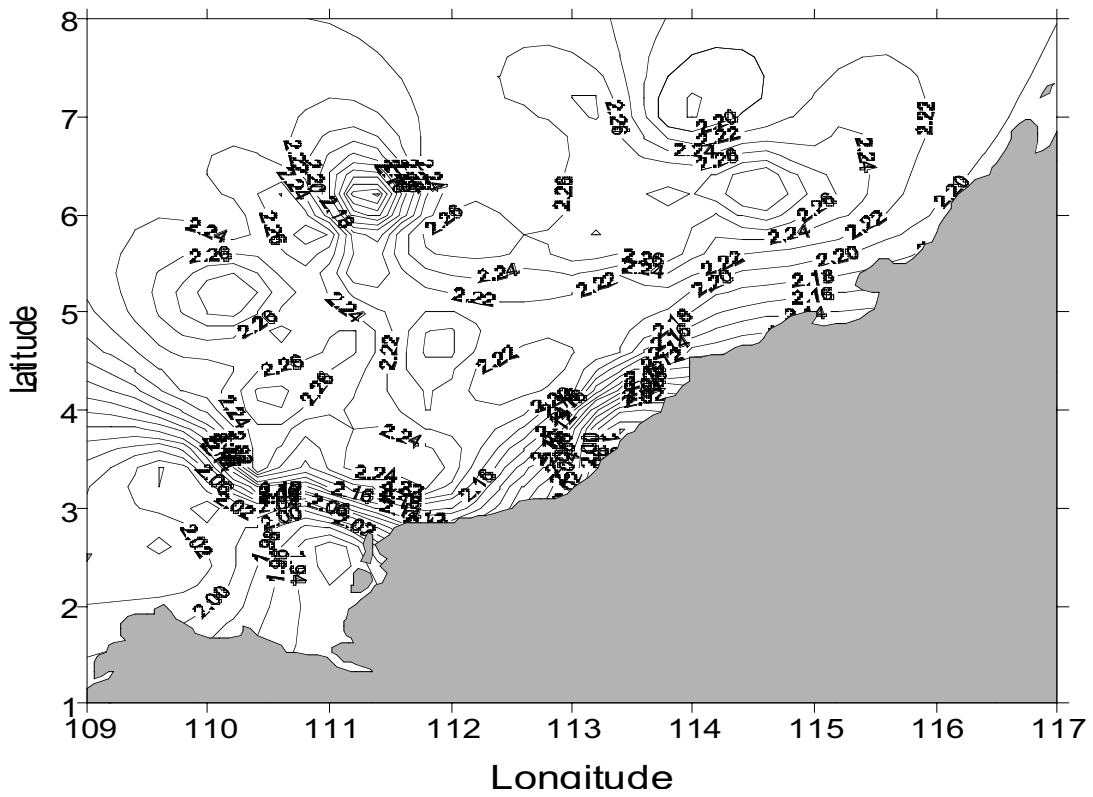
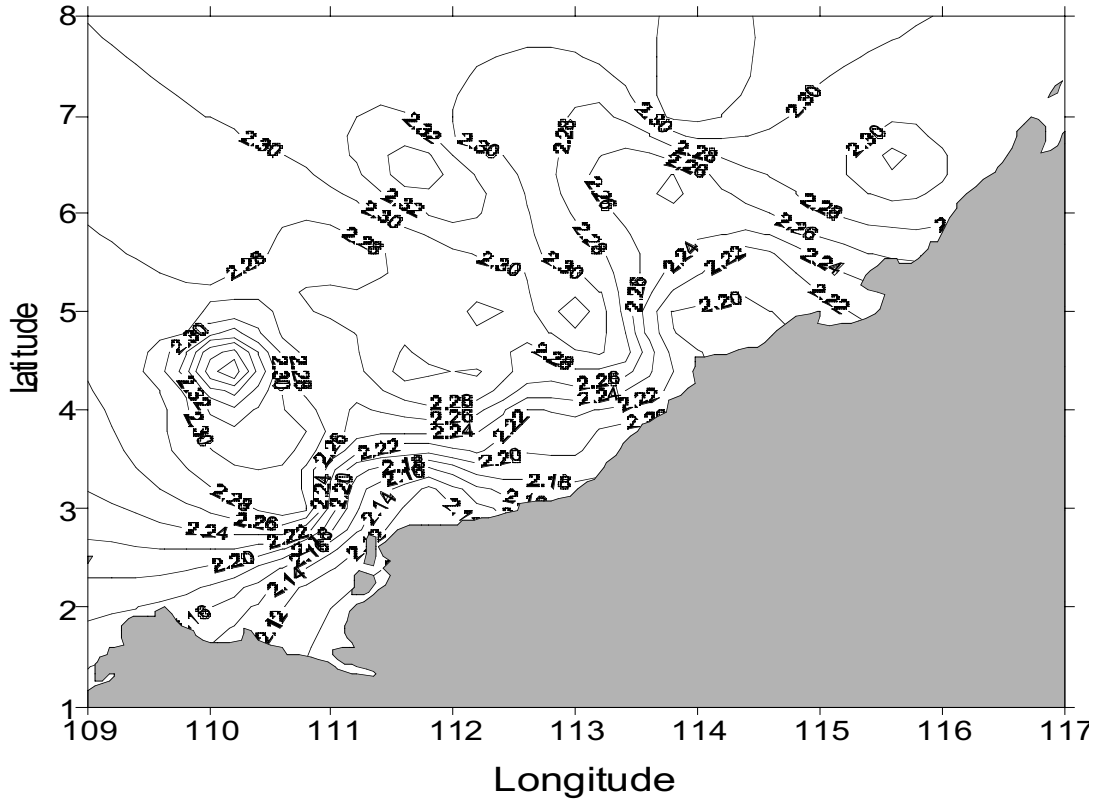


Fig. 7A Total alkalinity at sea surface

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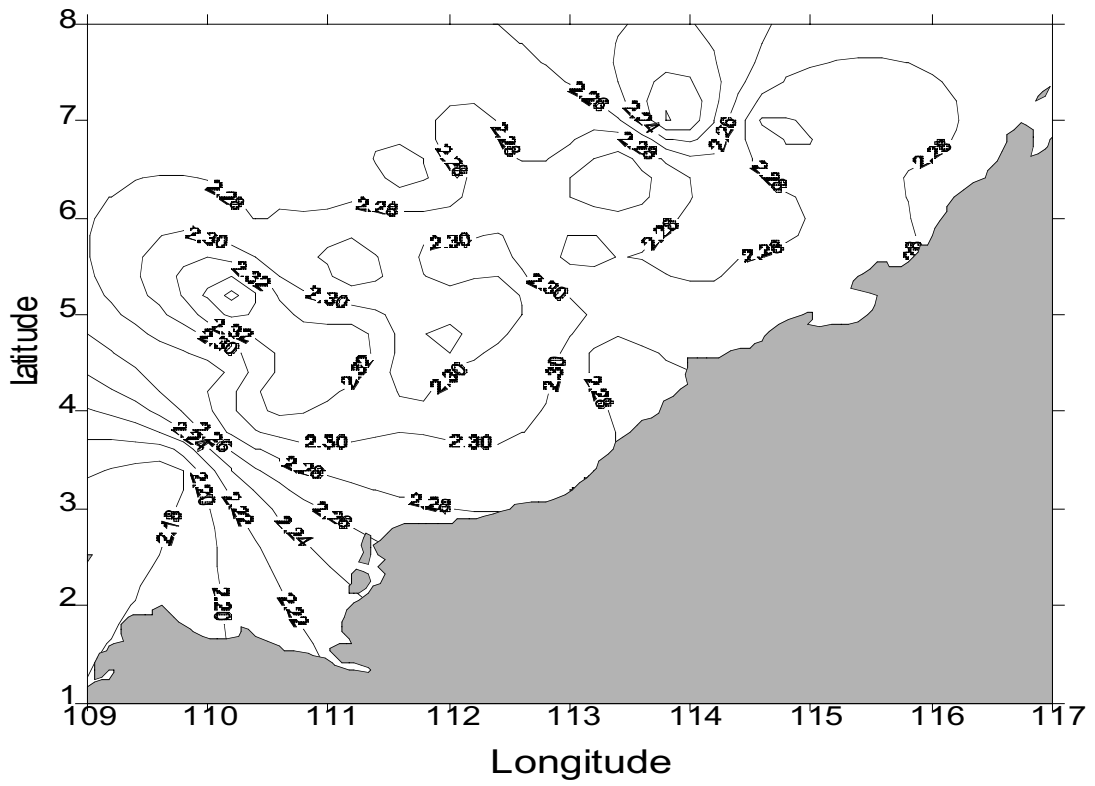
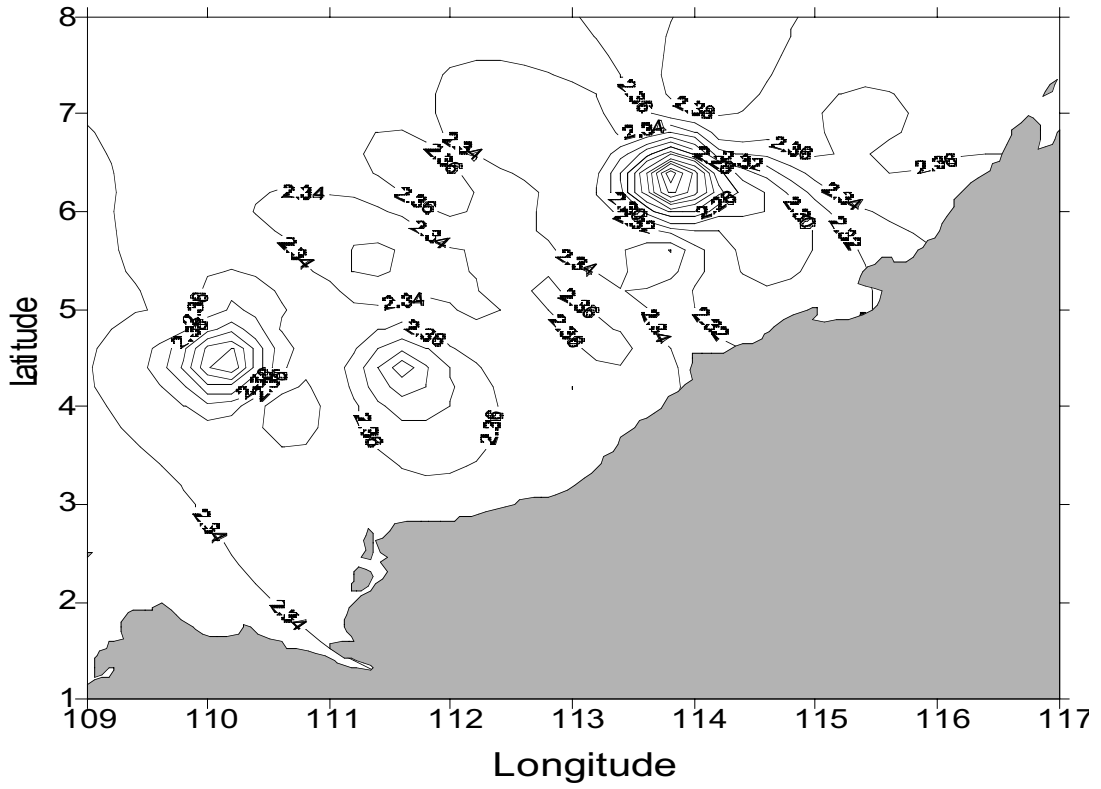


Fig. 7B Total alkalinity on the 23.0 kg/m<sup>3</sup> isopycnal surface



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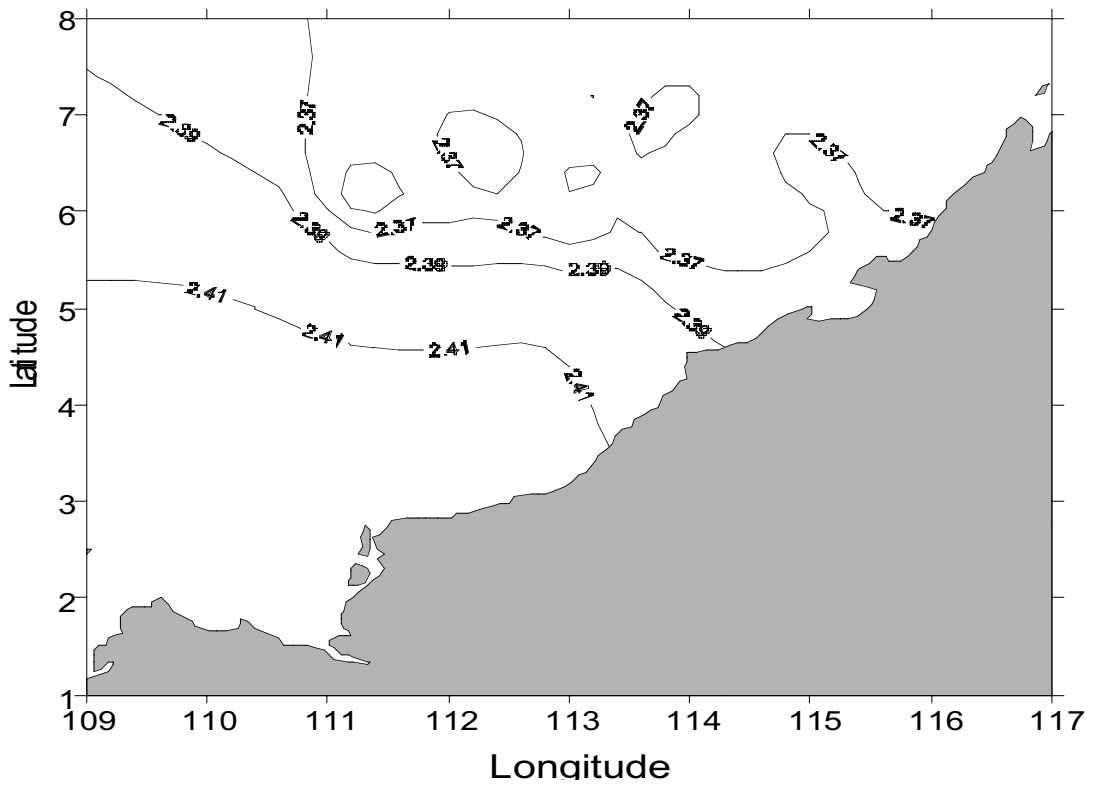
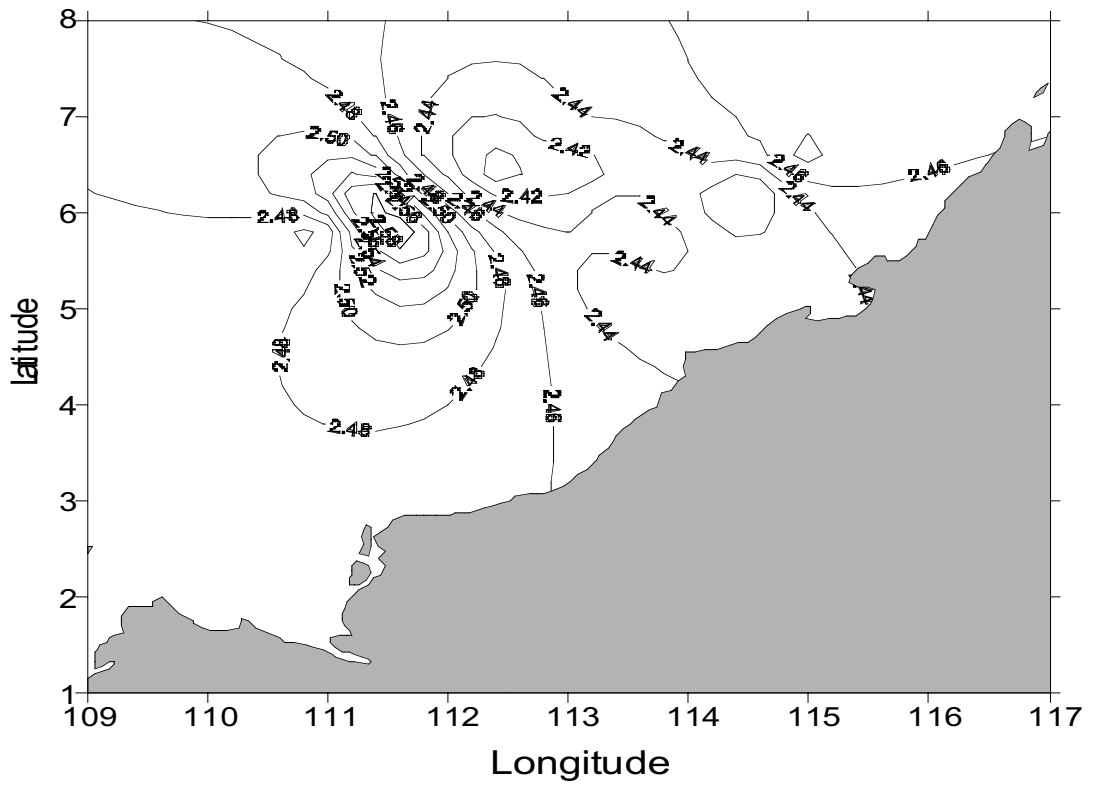


Fig. 7D Total alkalinity on the 27.0 kg/m<sup>3</sup> isopycnal surface

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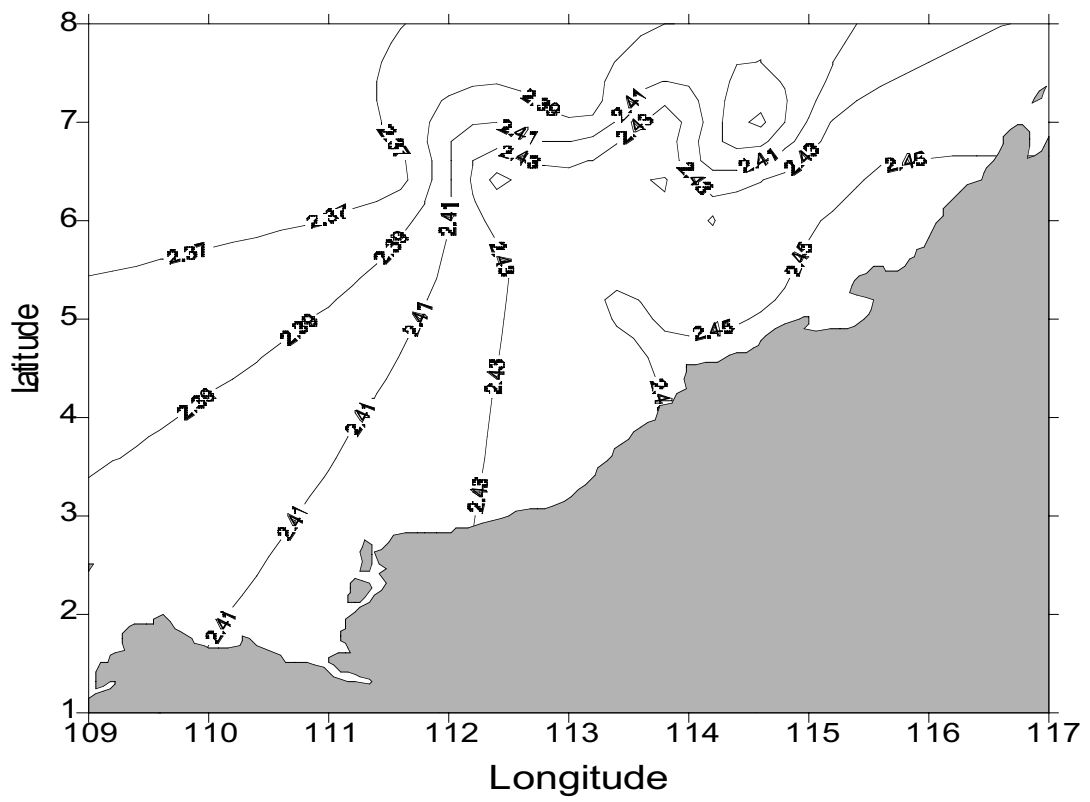
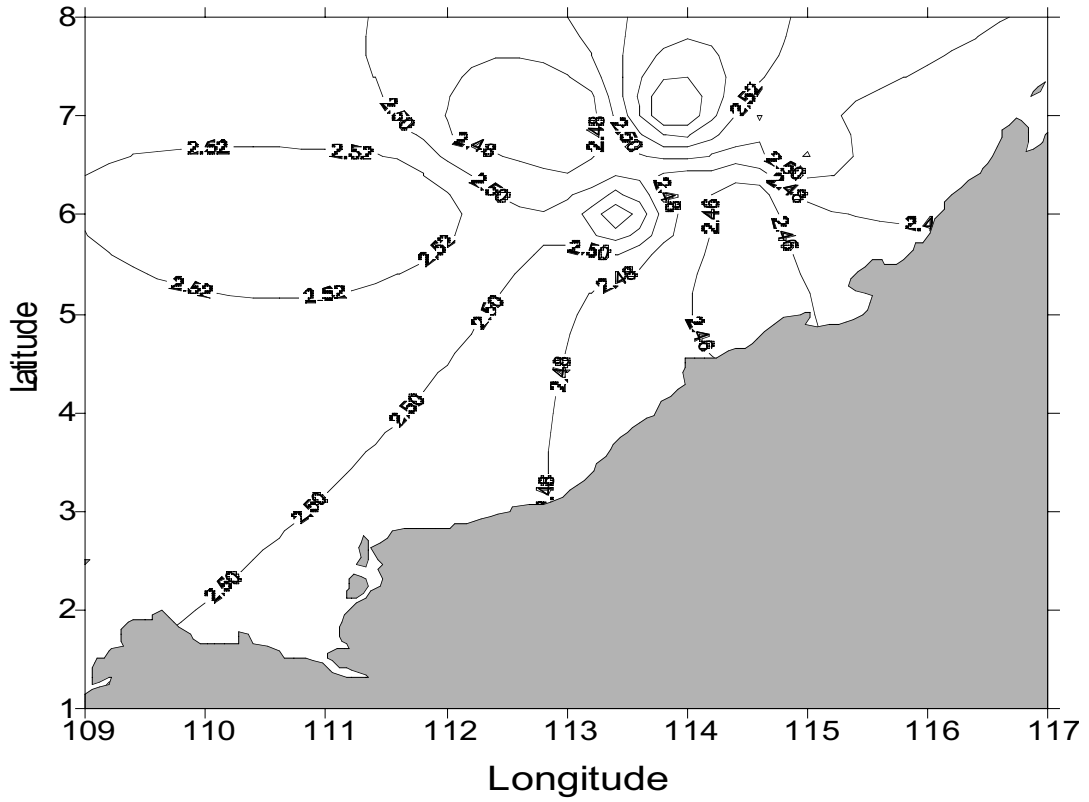


Fig. 7E Total alkalinity on the 27.5 kg/m<sup>3</sup> isopycnal surface

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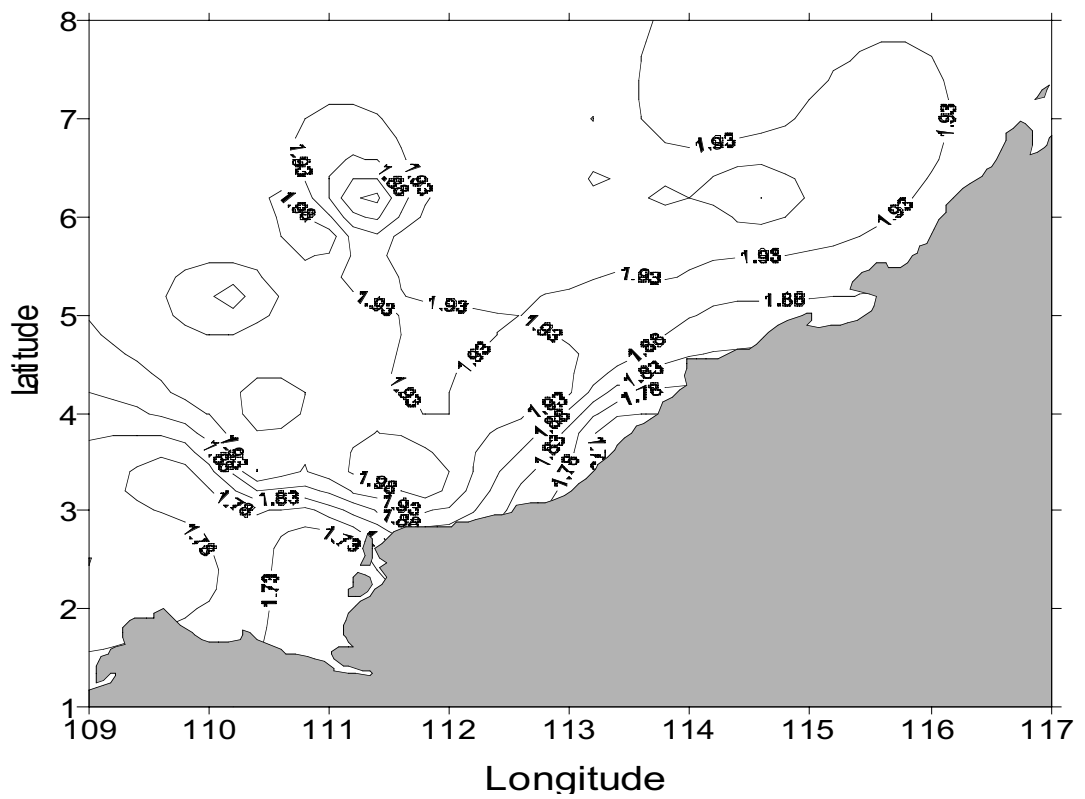
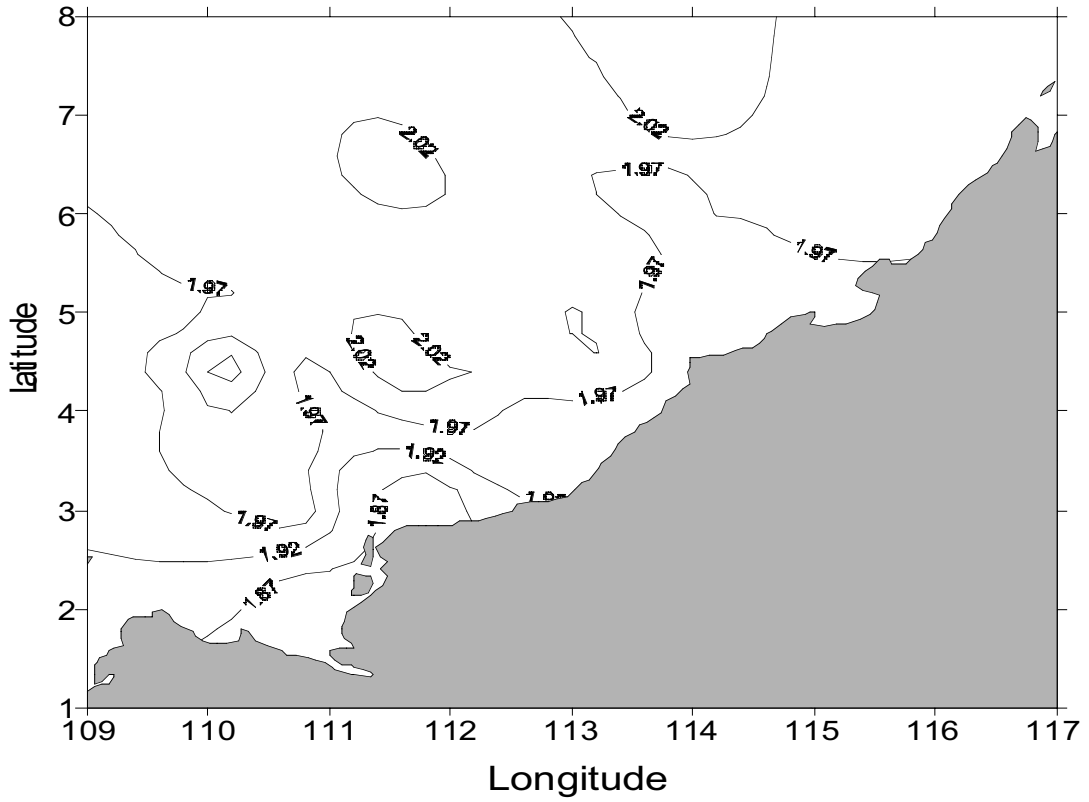


Fig. 8A Total dissolved inorganic carbon at sea surface

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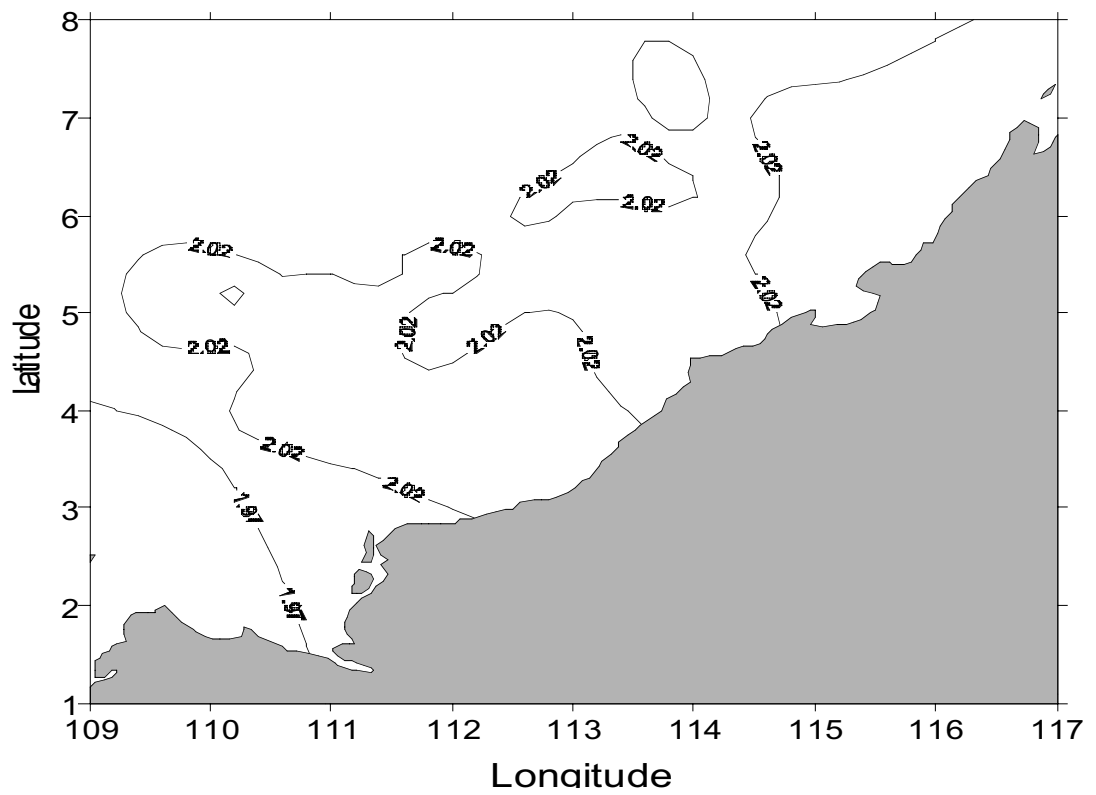
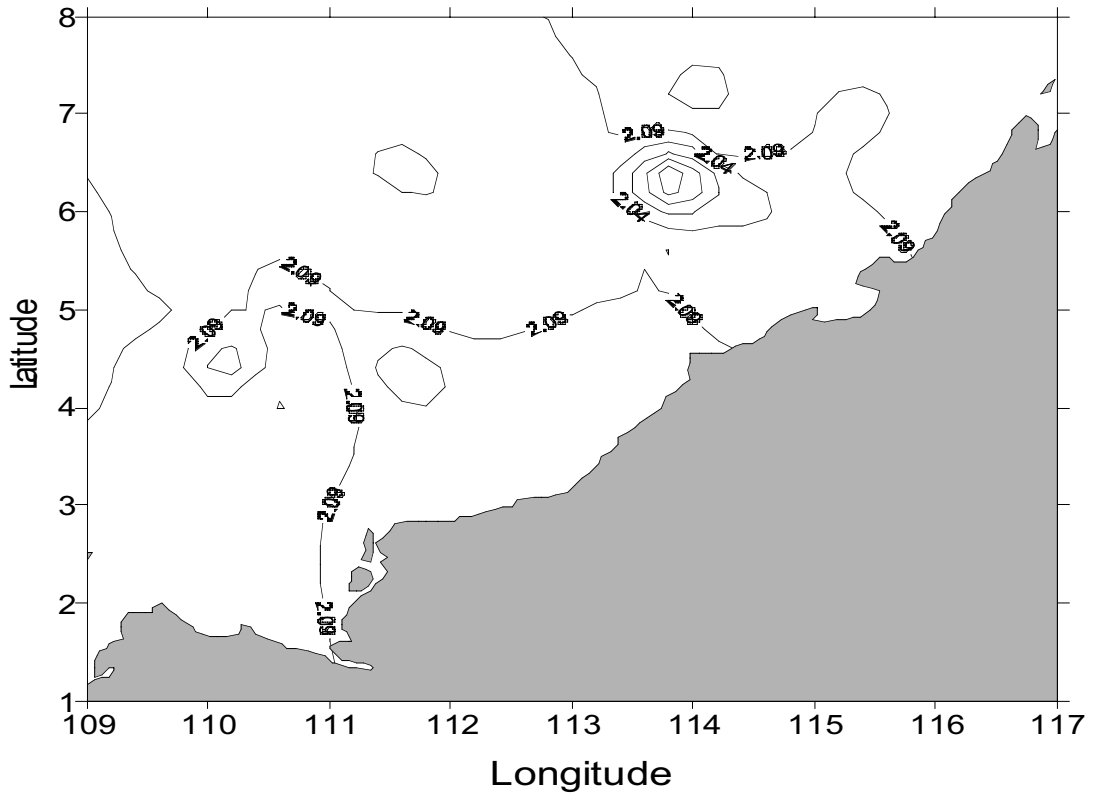


Fig. 8B Total dissolved inorganic carbon on the 23.0 kg/m<sup>3</sup> isopycnal surface



S2/OG4<ANOND>

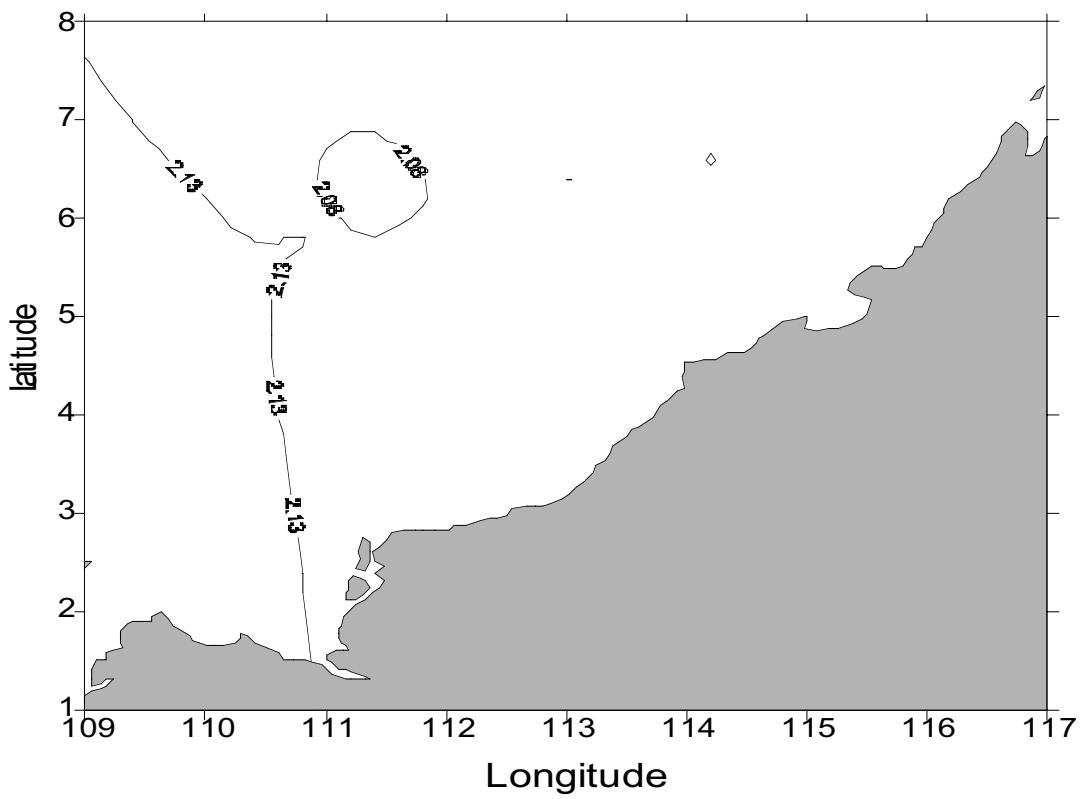
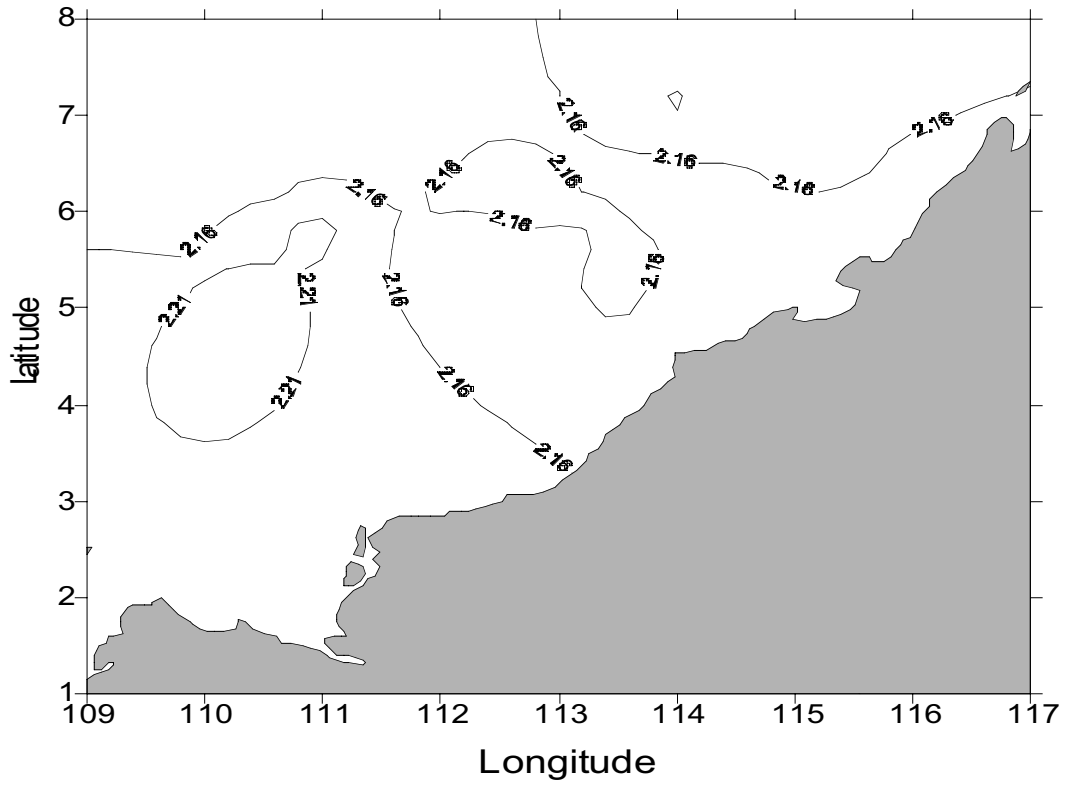


Fig. 8C Total dissolved inorganic carbon on the 27.0 kg/m<sup>3</sup> isopycnal surface

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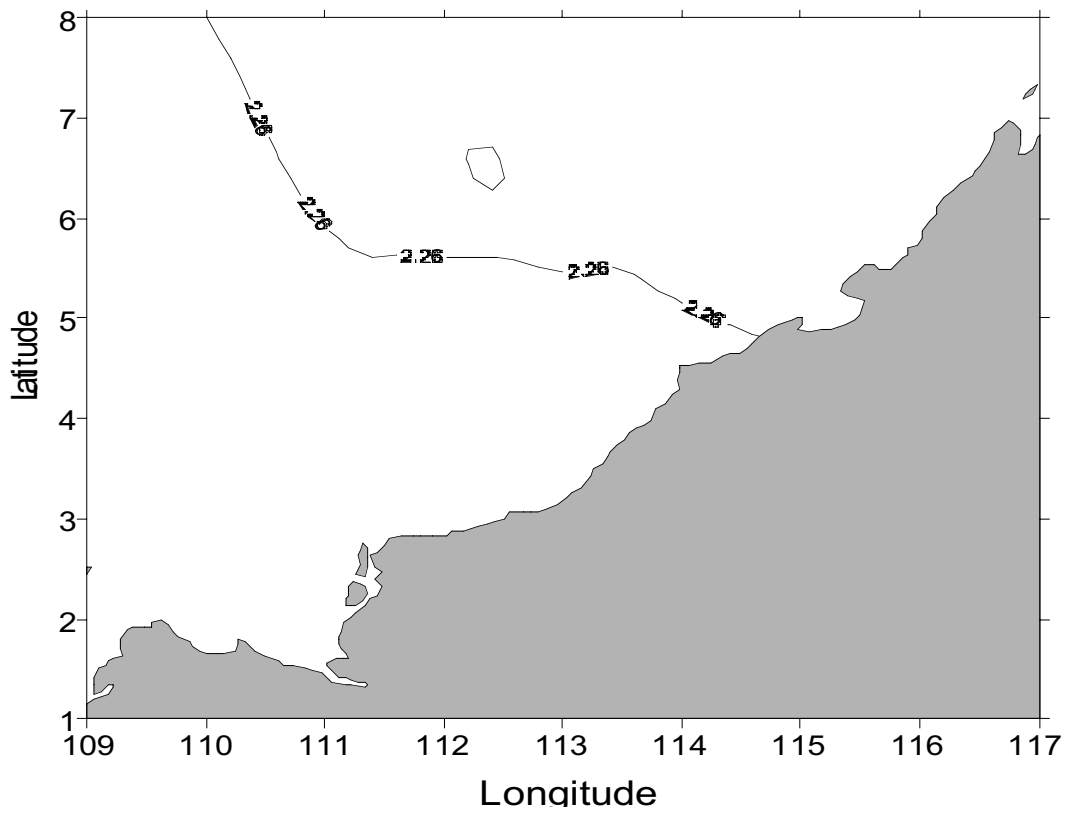
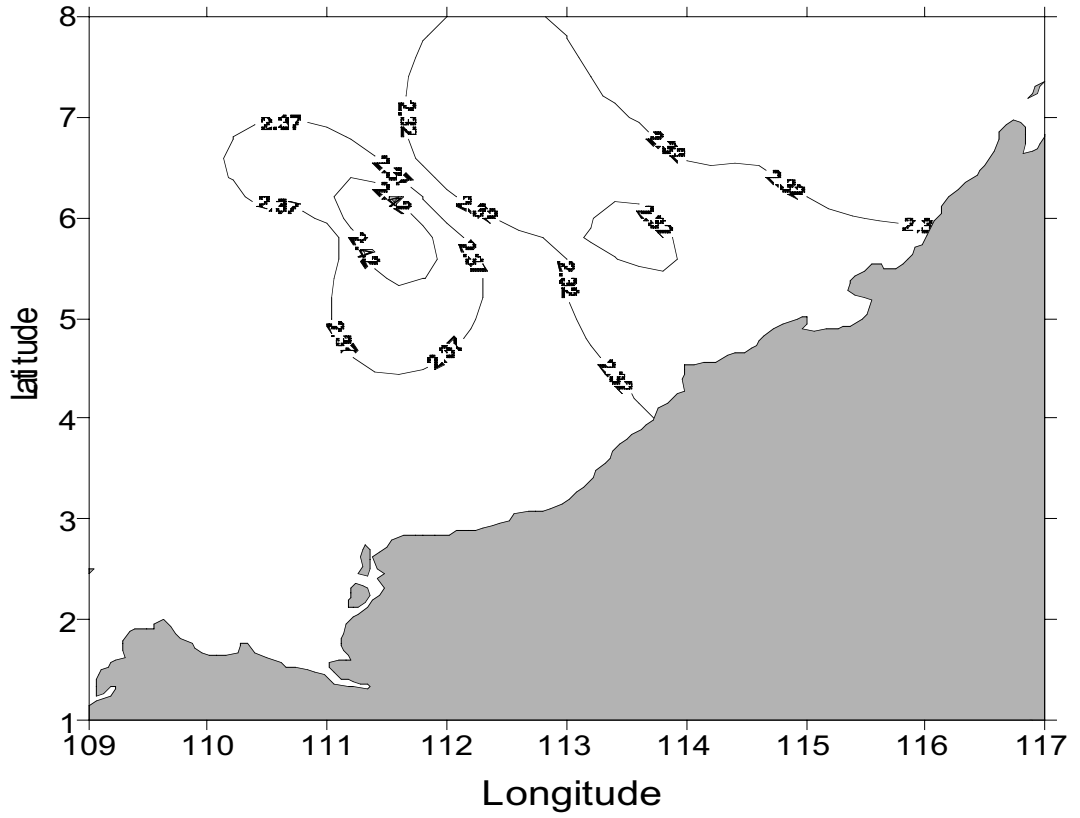


Fig. 8D Total dissolved inorganic carbon on the 27.0 kg/m<sup>3</sup> isopycnal surface

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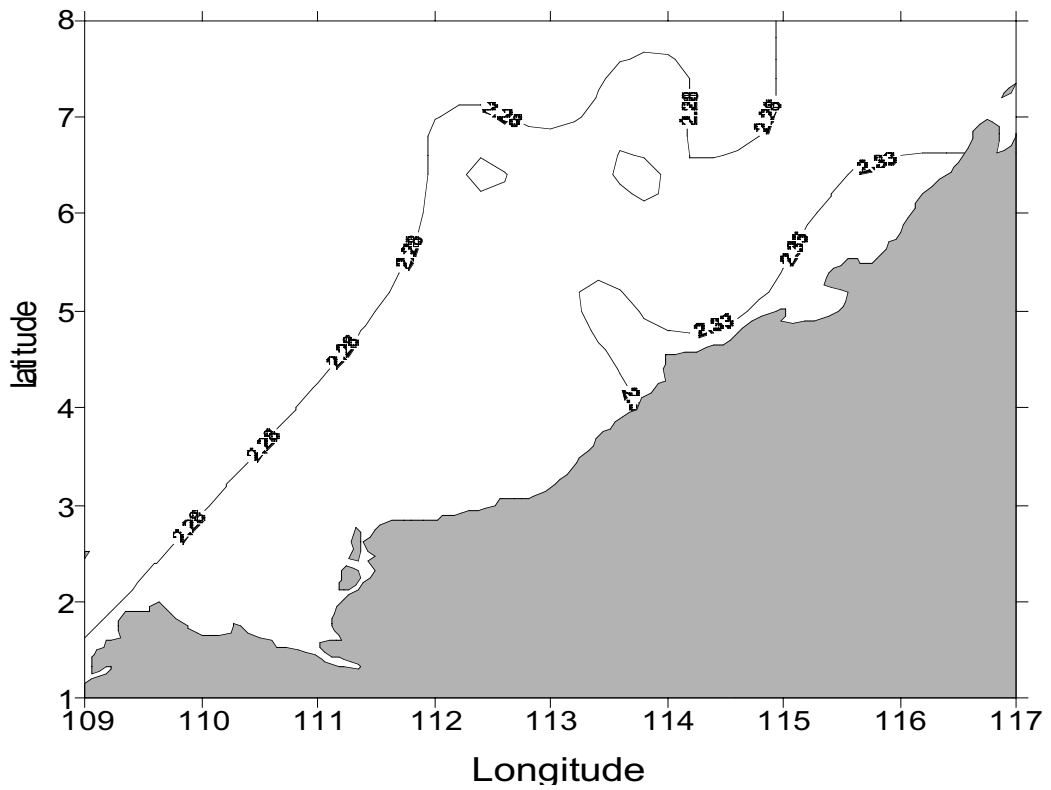
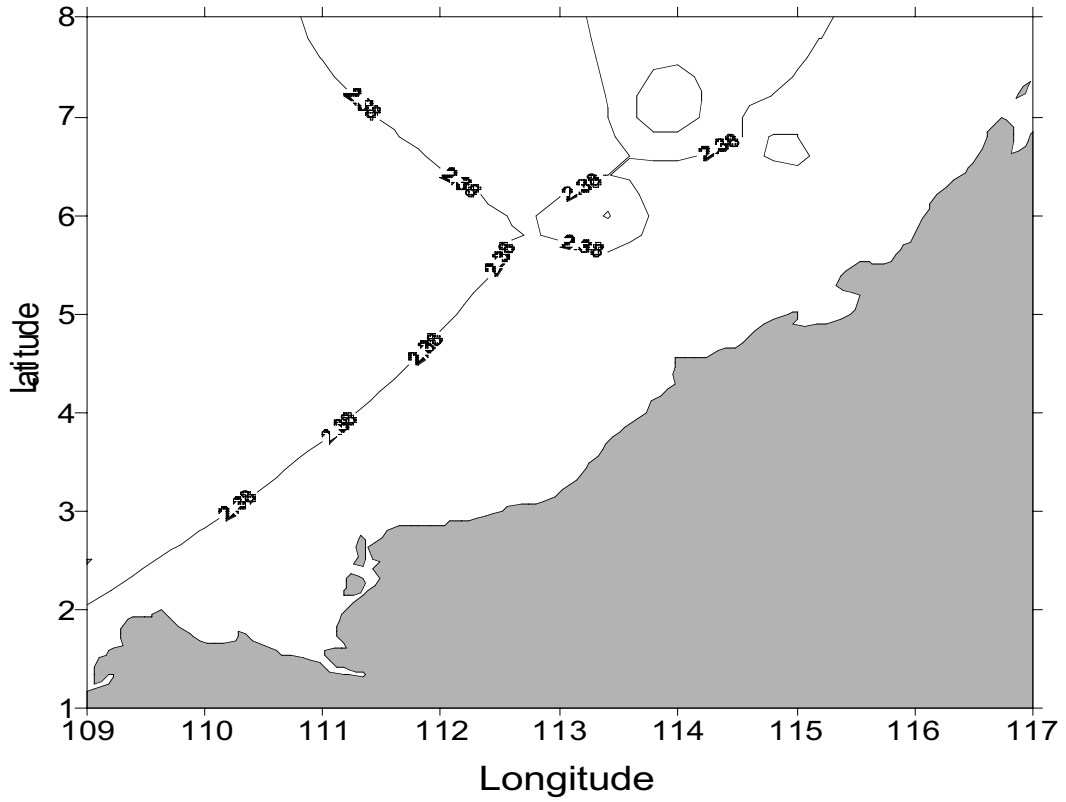


Fig. 8E Total dissolved inorganic carbon on the 27.5 kg/m<sup>3</sup> isopycnal surface

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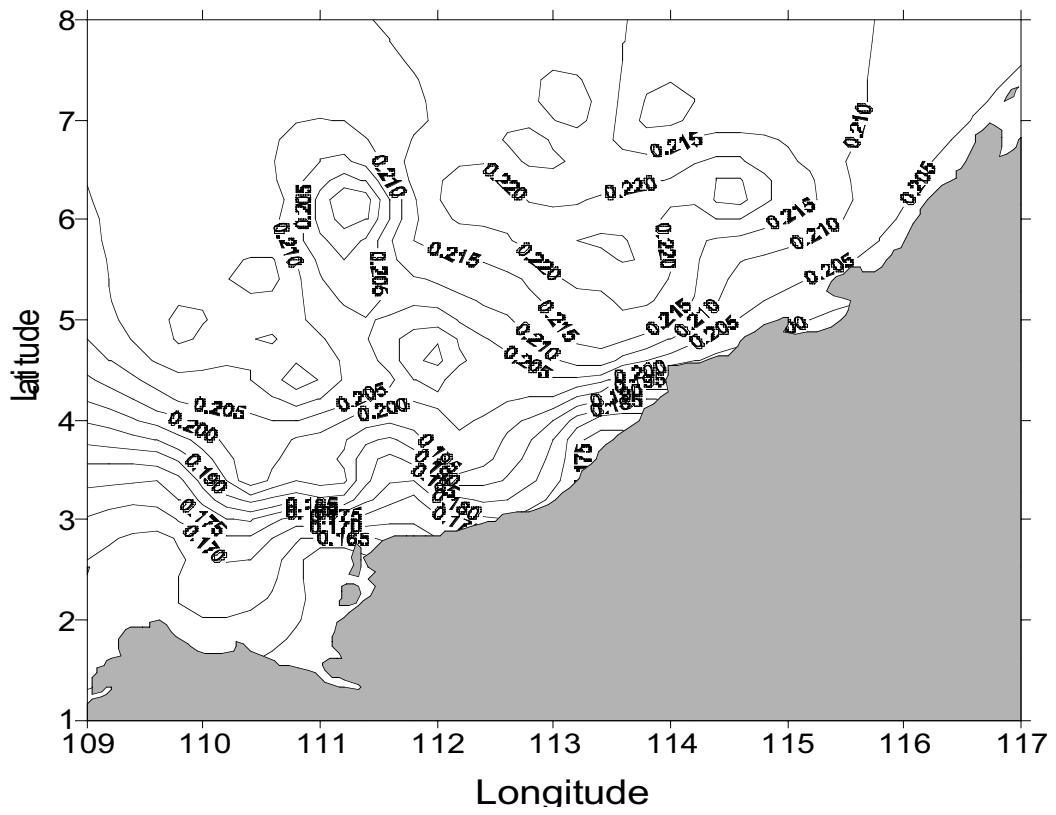
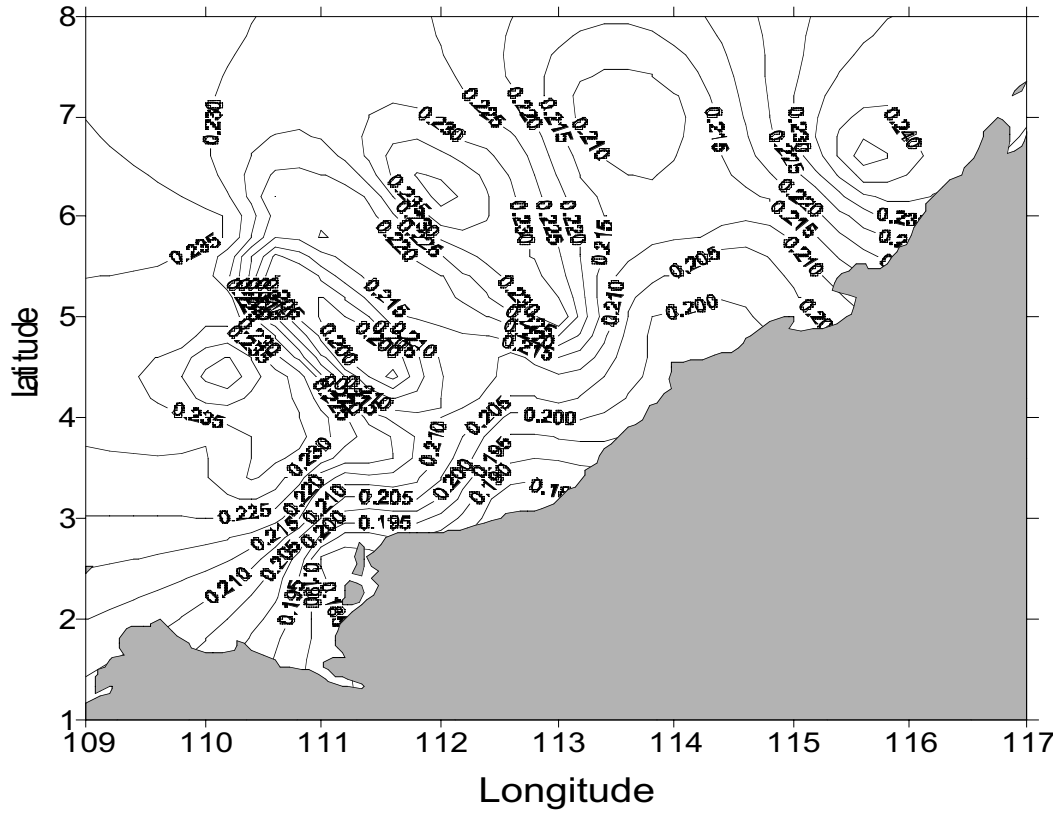


Fig. 9A Dissolved carbonate at sea surface

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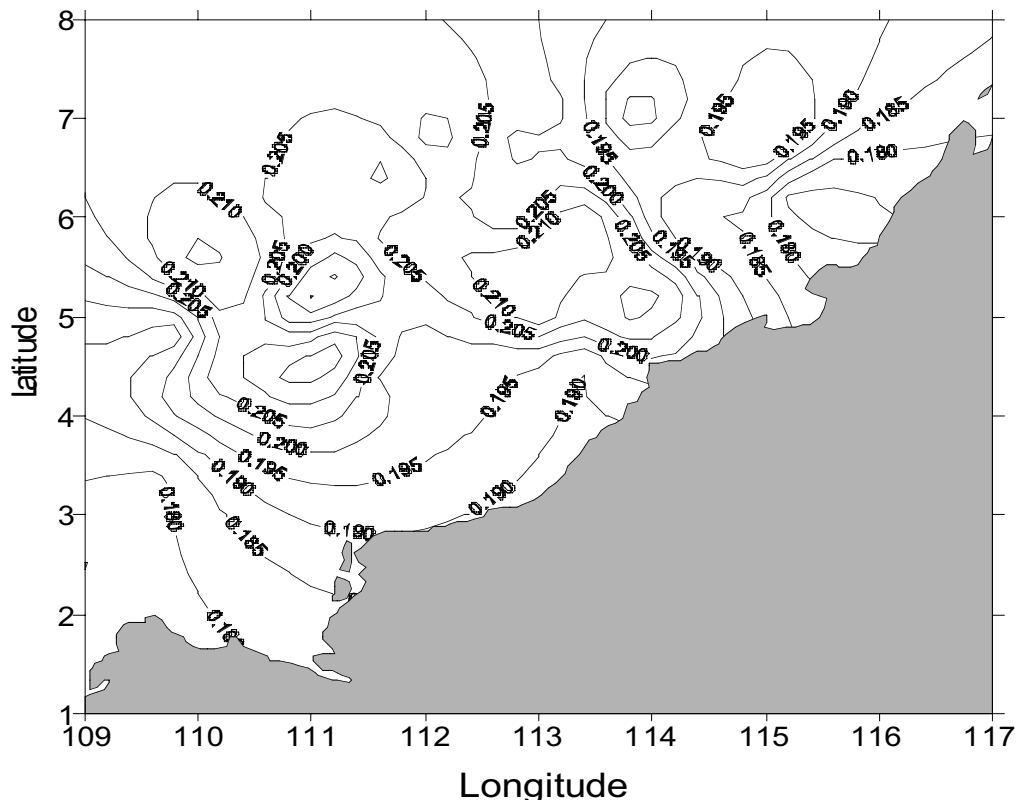
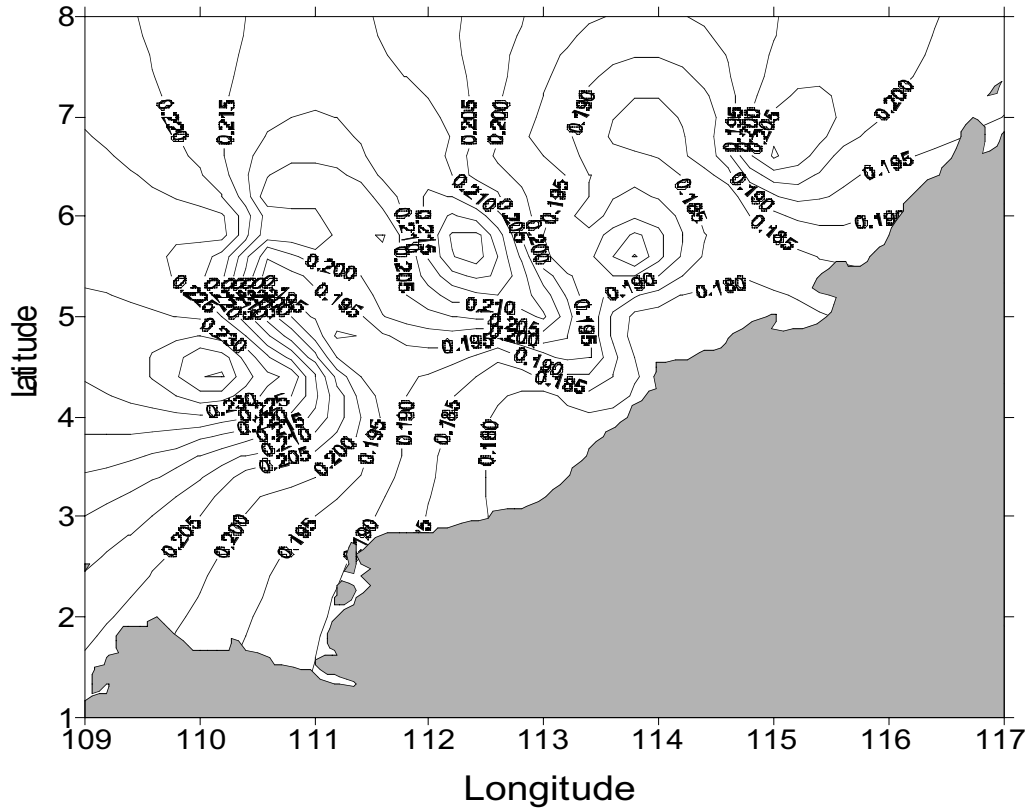


Fig. 9B Dissolved carbonate on the  $23.0\text{kg/m}^3$  isopycnal surface

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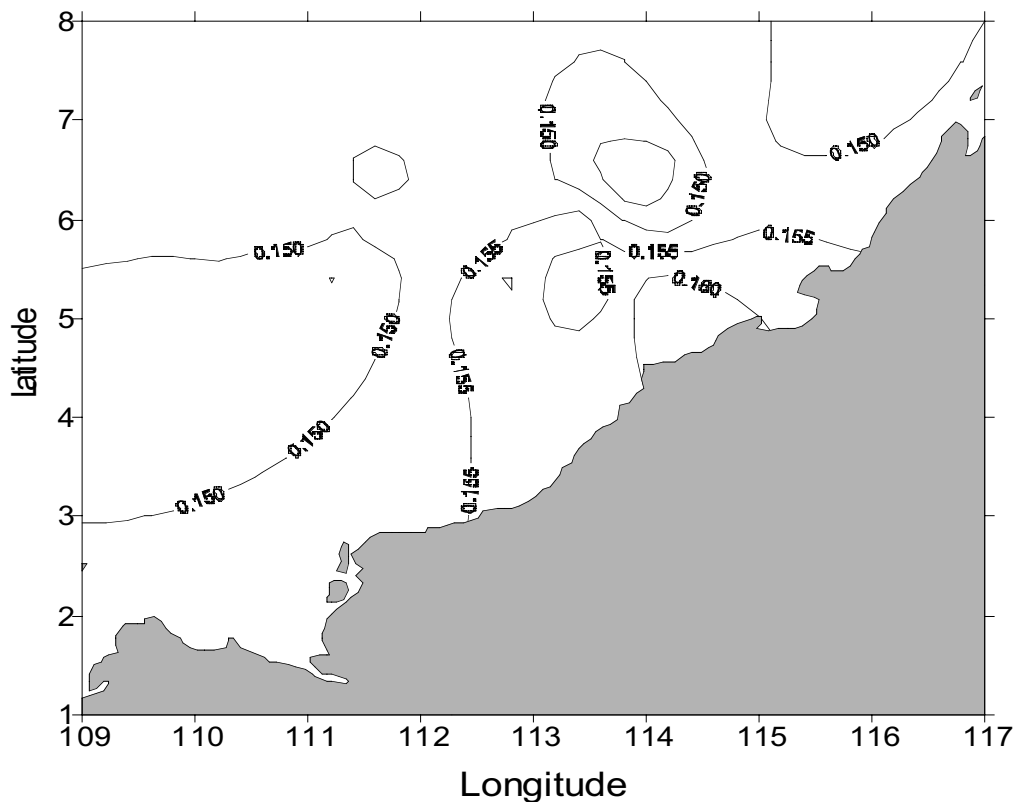
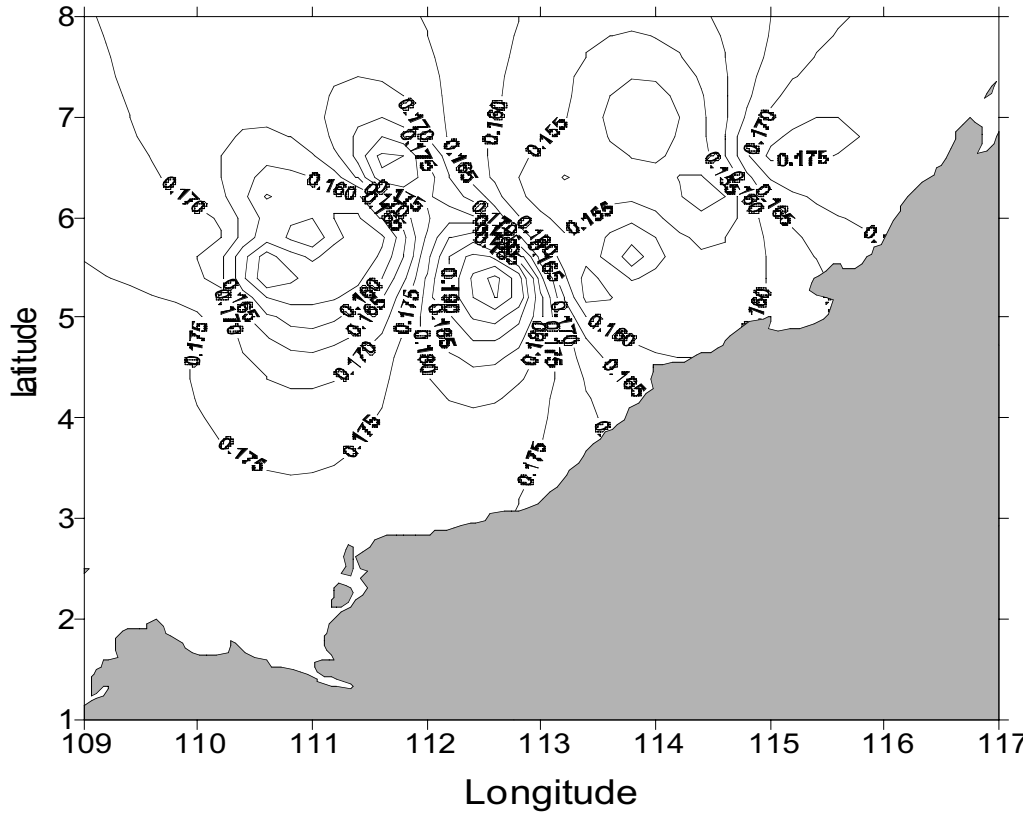


Fig. 9C Dissolved carbonate on the 25.0kg/m<sup>3</sup> isopycnal surface

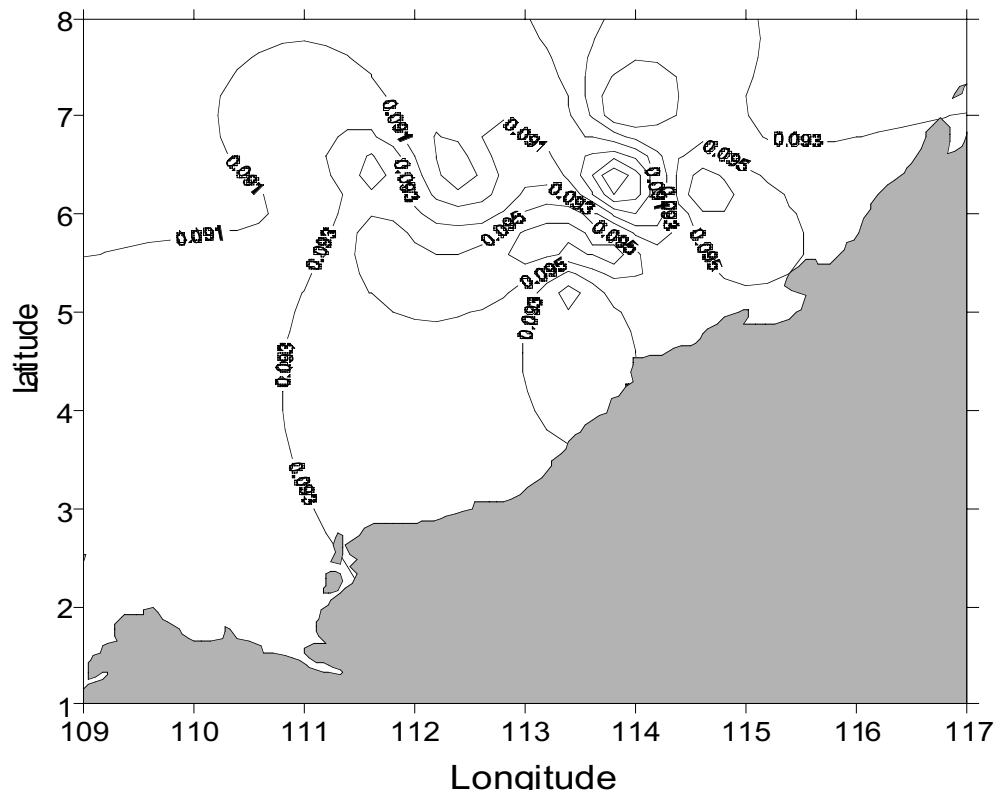
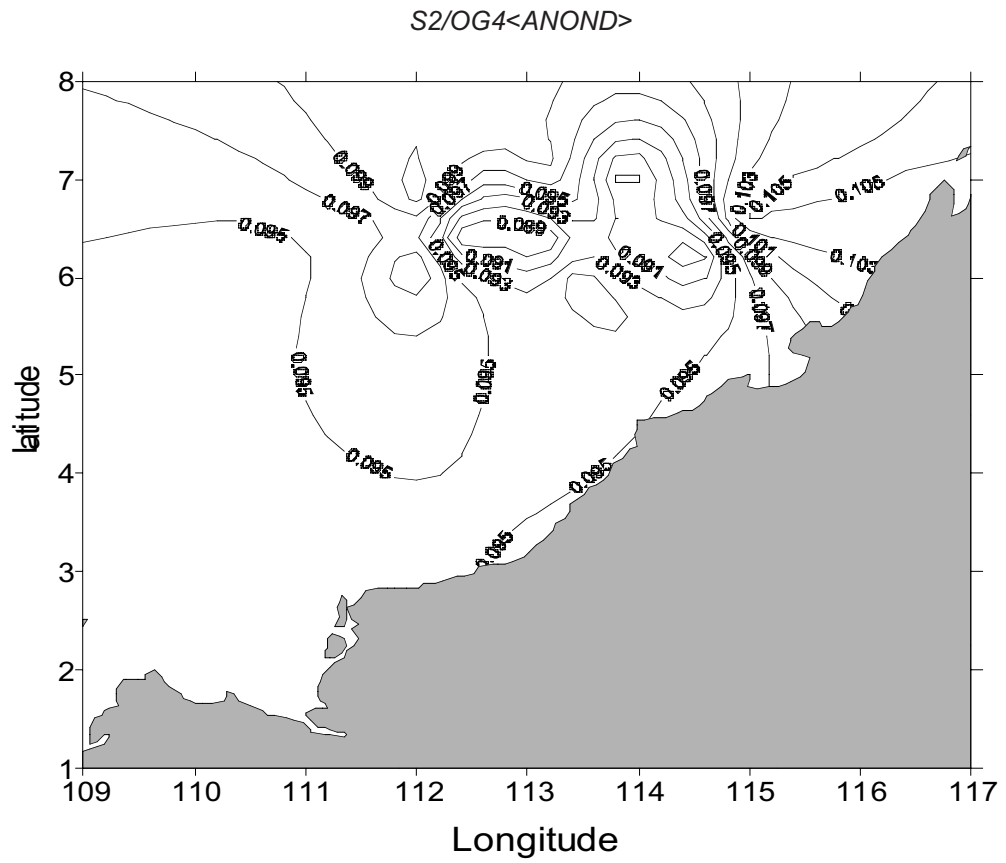


Fig. 9D Dissolved carbonate on the 27.0kg/m<sup>3</sup> isopycnal surface

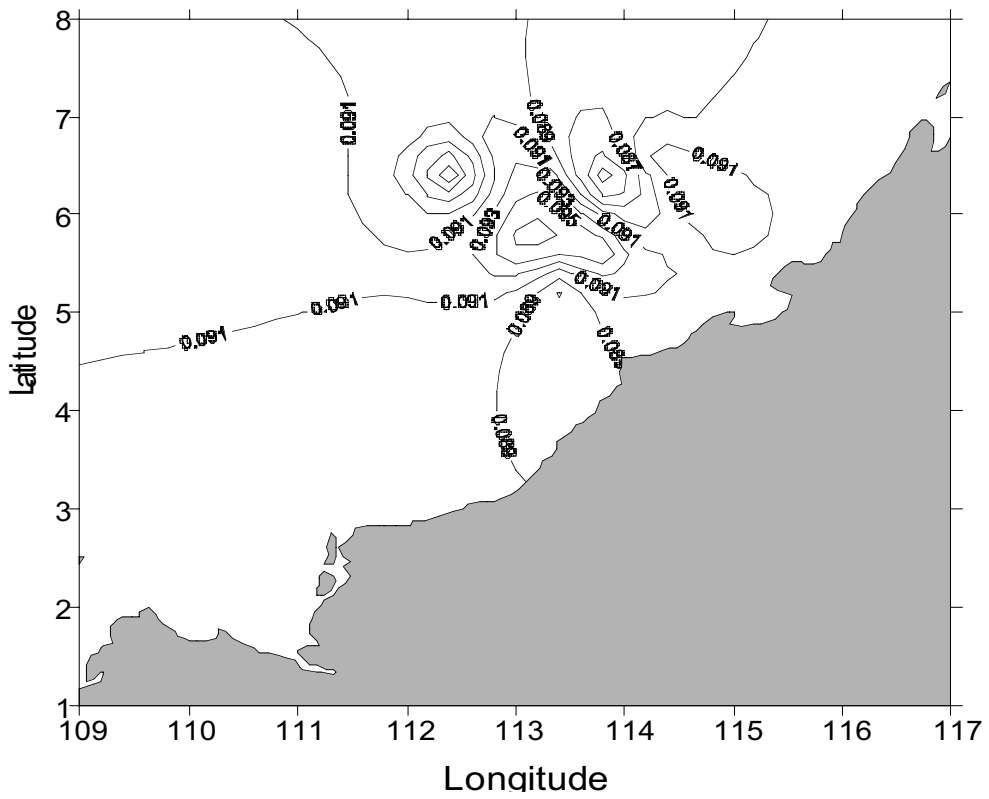
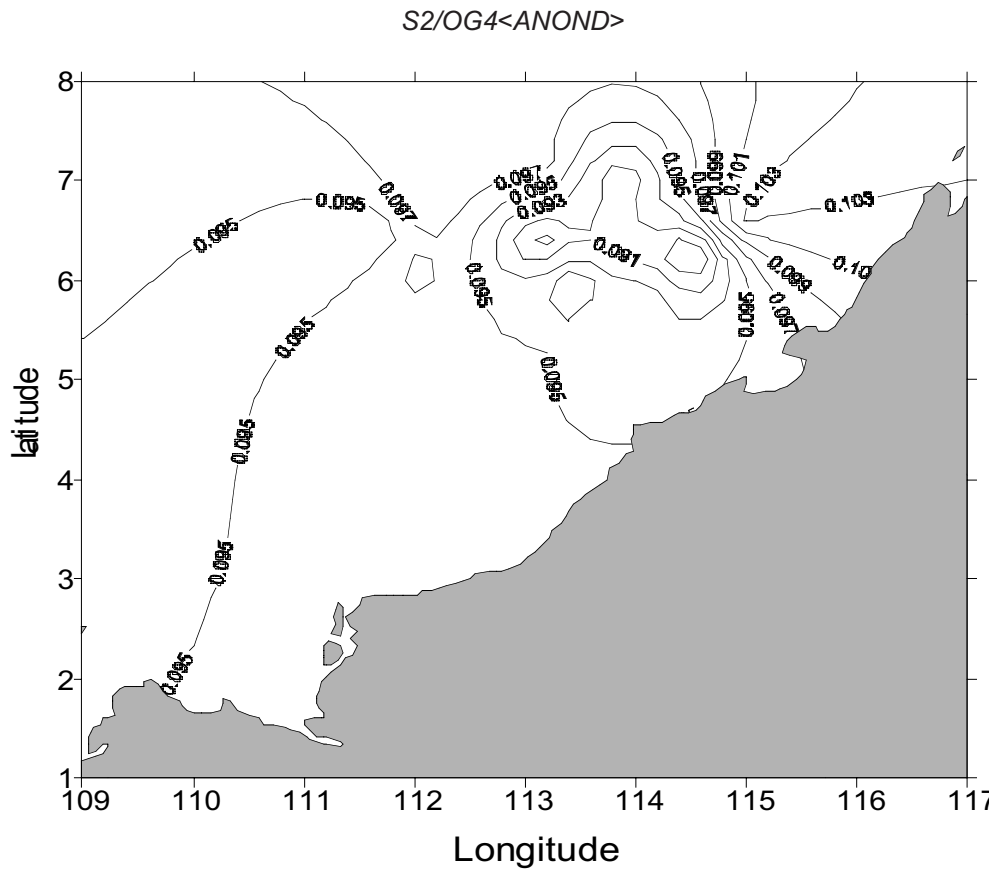


Fig. 9E Dissolved carbonate on the 27.50kg/m<sup>3</sup> isopycnal surface



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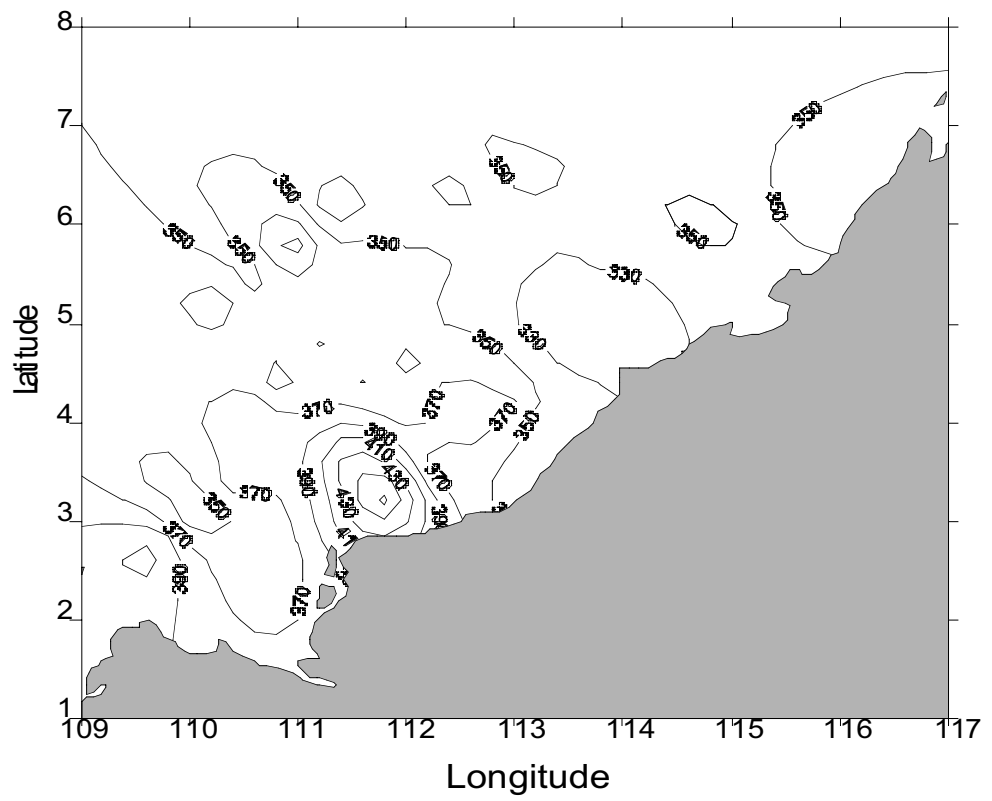
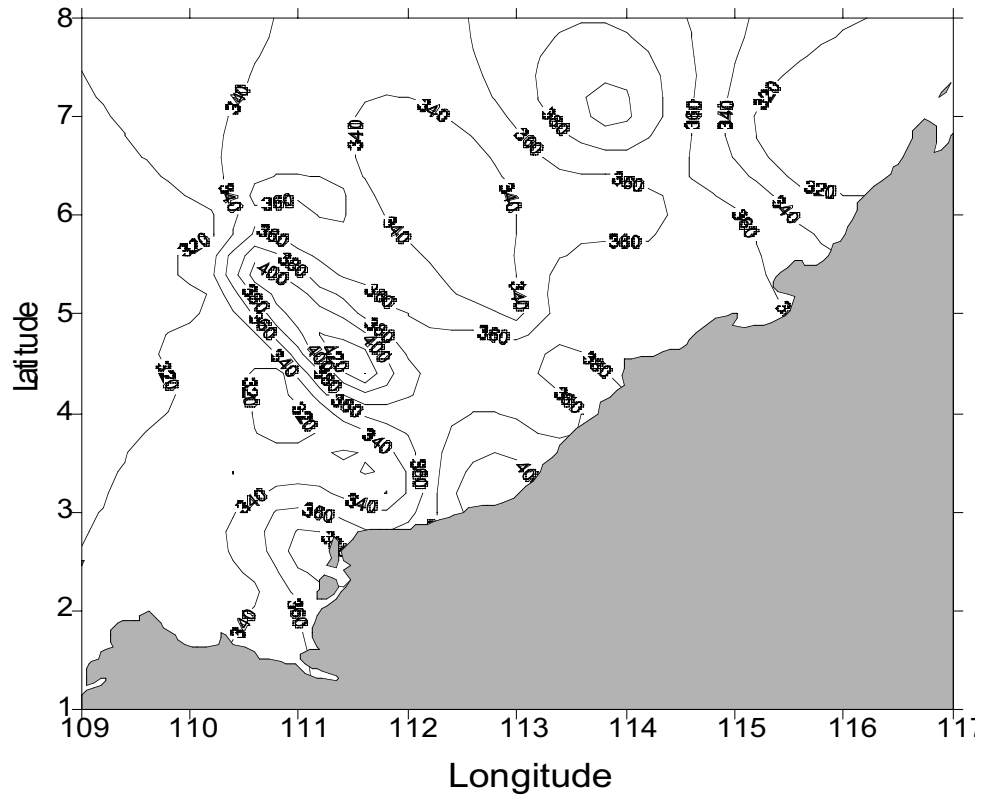


Fig. 10A Carbon dioxide partial pressure (uatm) at the sea

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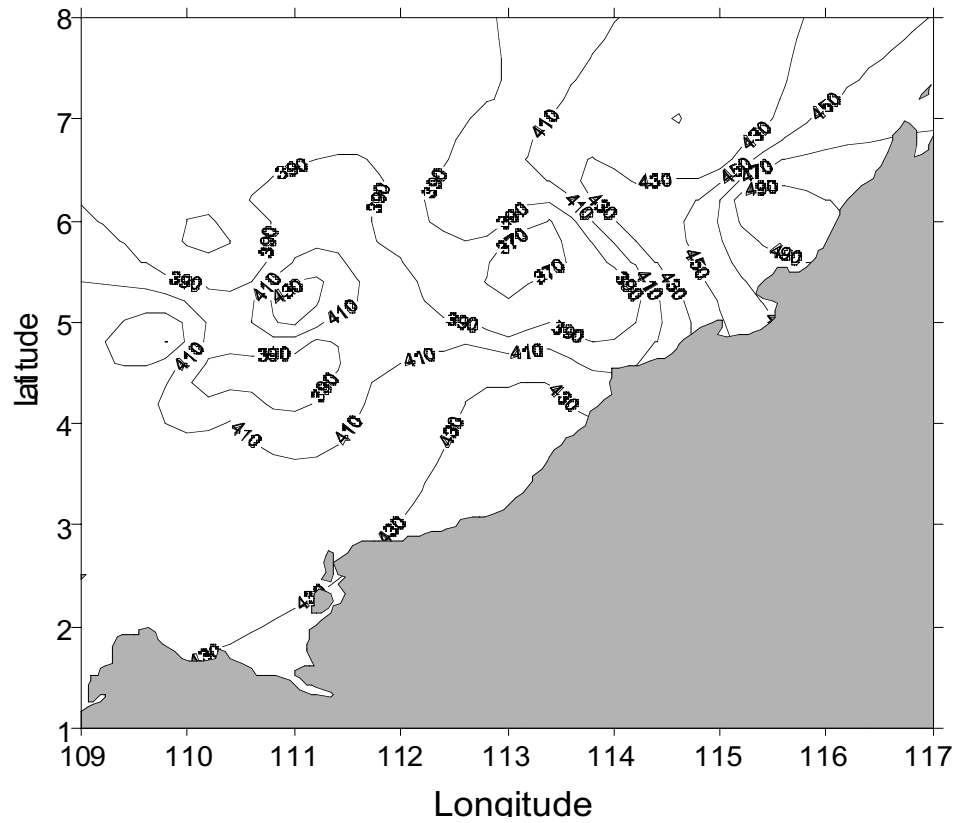
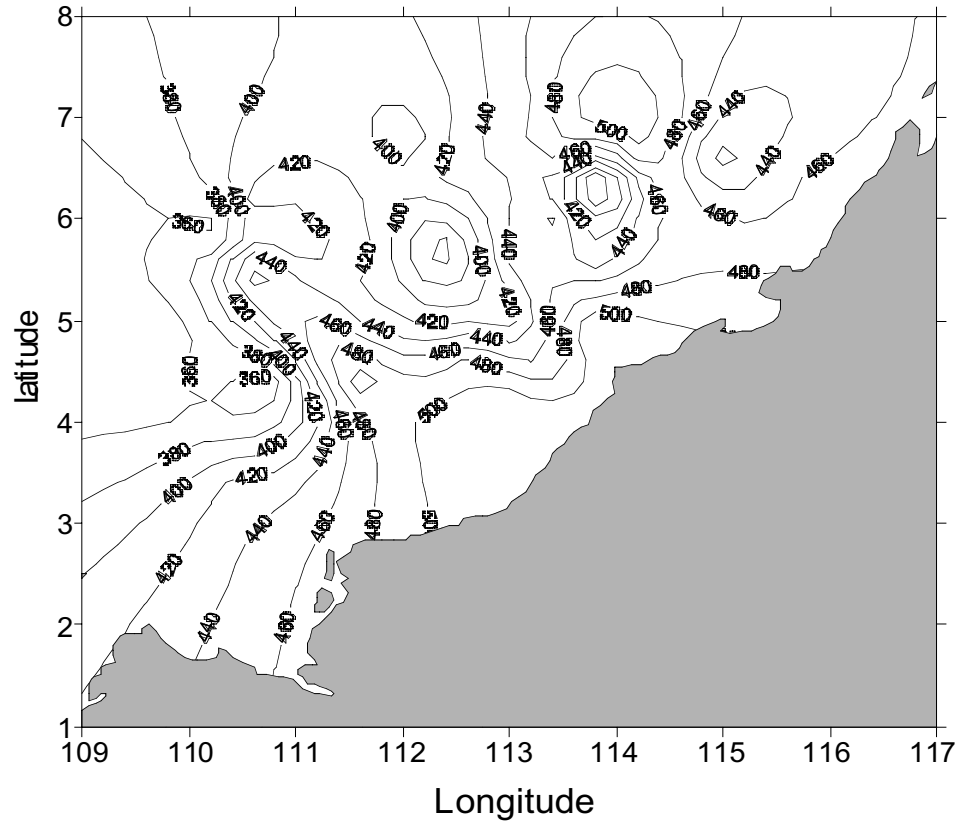


Fig. 10B Carbon dioxide partial pressure (uatm) on the  $23.0 \text{ kg/m}^3$  isopycnal surface

S2/OG4<ANOND>

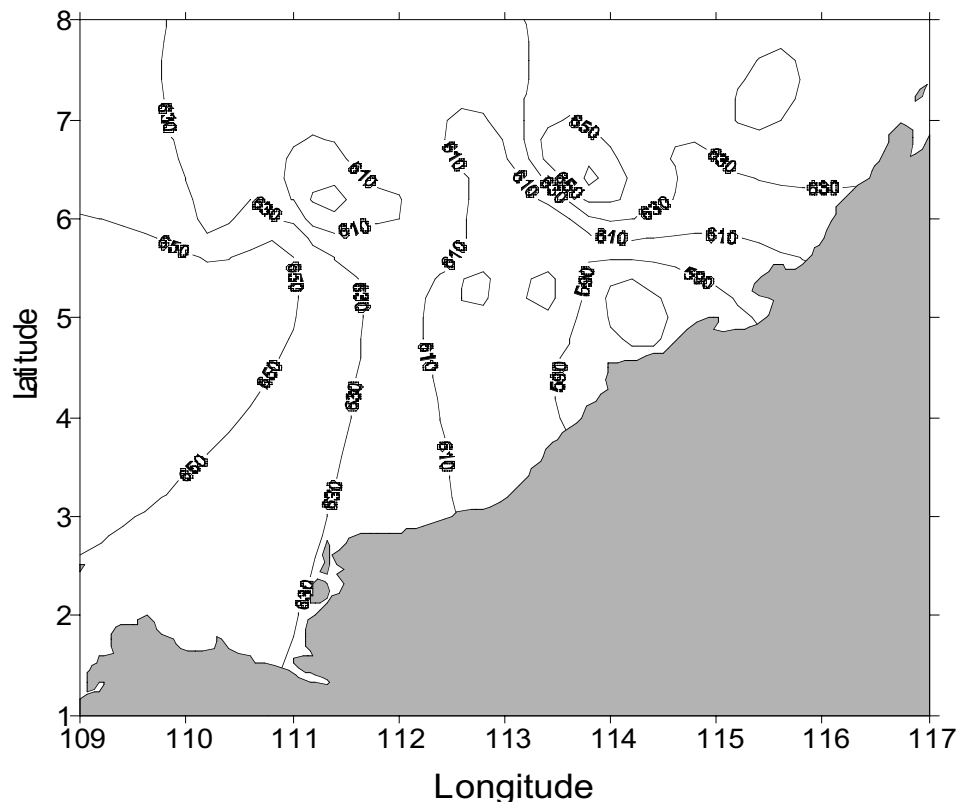
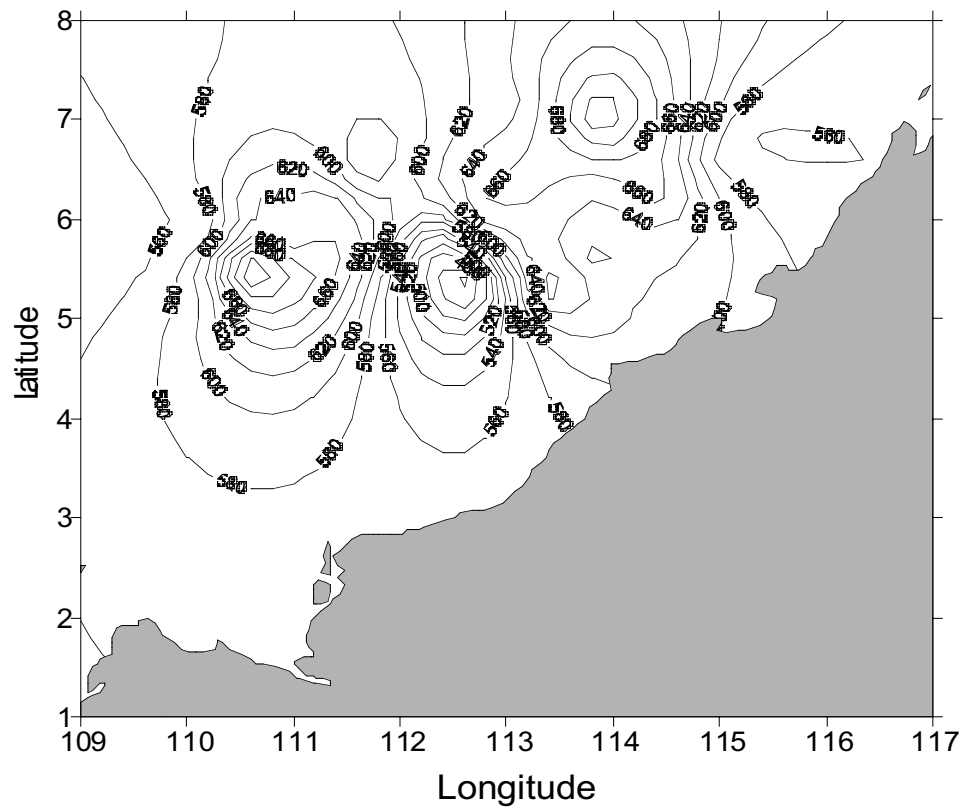


Fig. 10C Carbon dioxide partial pressure (uatm) on the 25.0 kg/m<sup>3</sup> isopycnal surface

S2/OG4<ANOND>

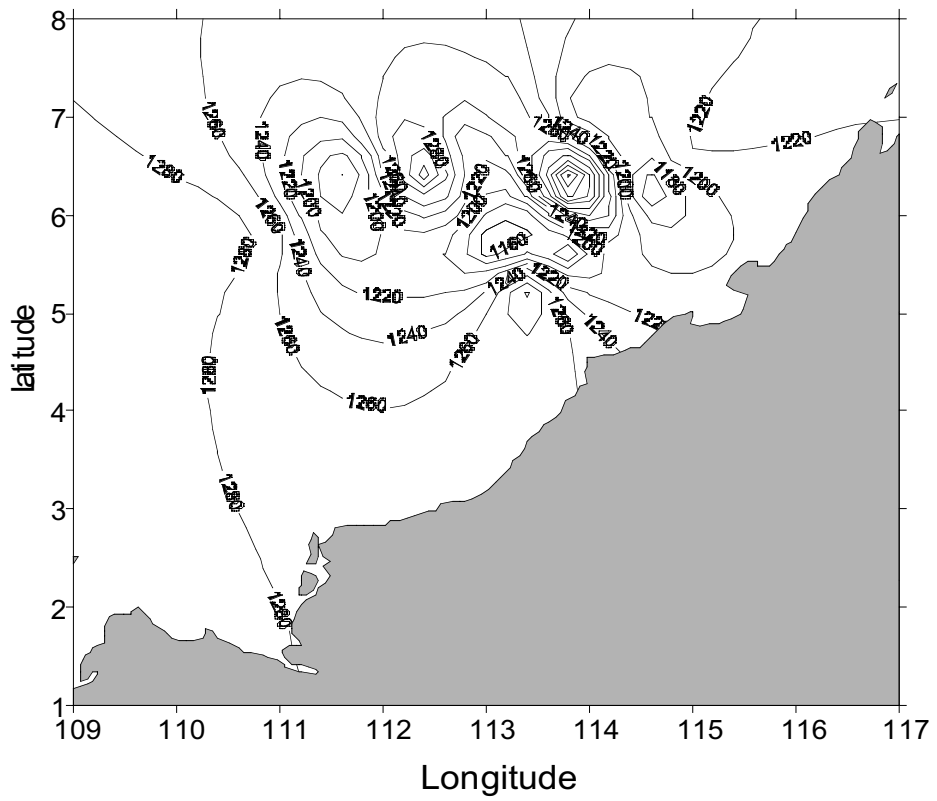
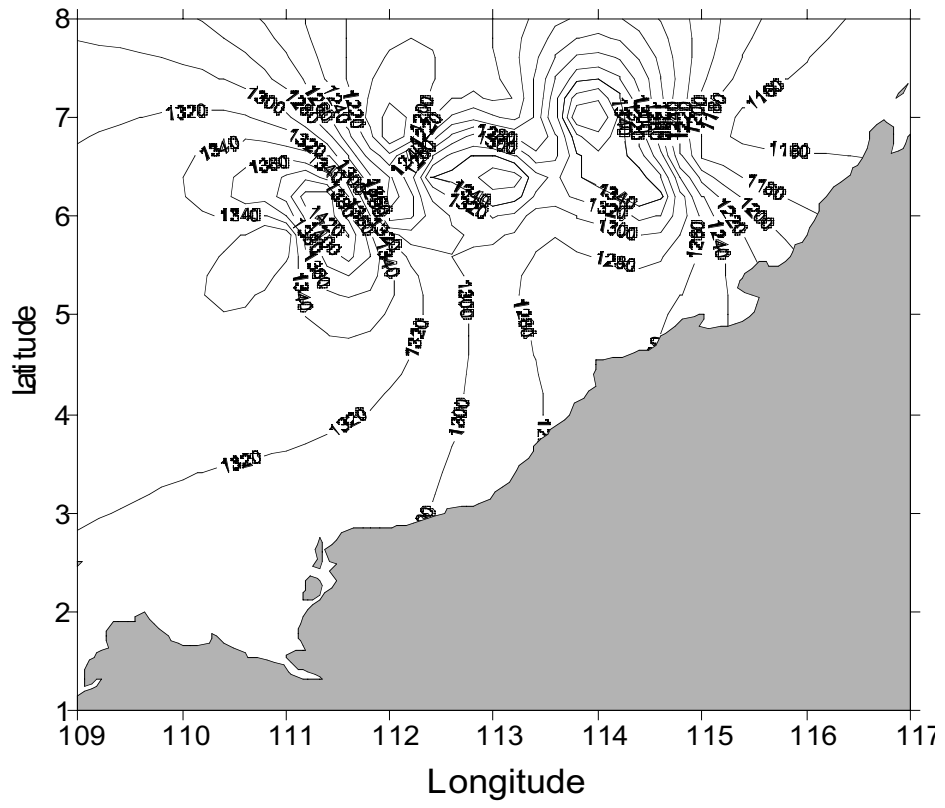


Fig. 10D Carbon dioxide partial pressure (uatm) on the 27.0 kg/m3 isopycnal surface

S2/OG4<ANOND>

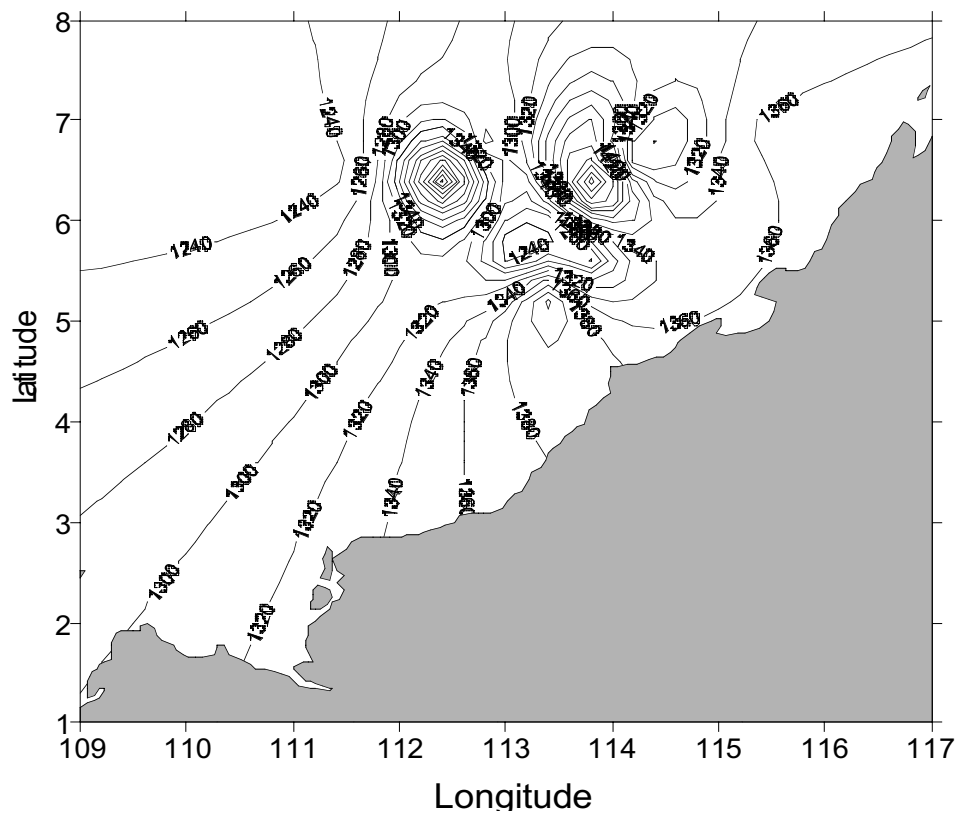
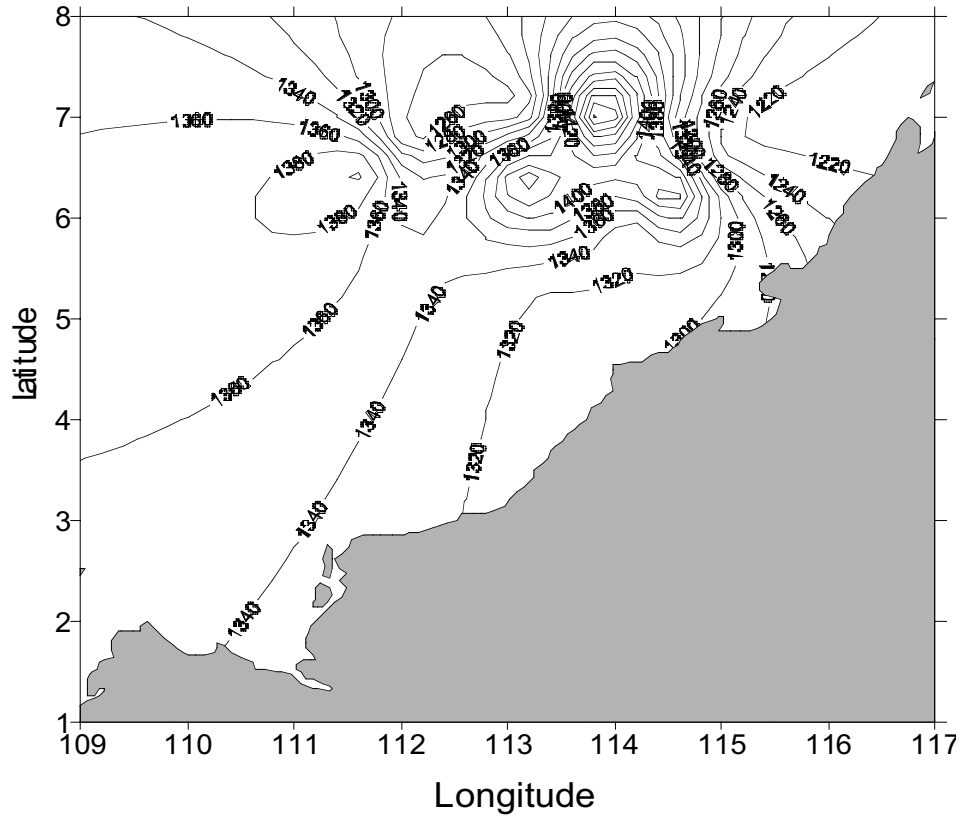


Fig. 10E Carbon dioxide partial pressure (uatm) on the 27.5 kg/m3 isopycnal surface

S2/OG4<ANOND>

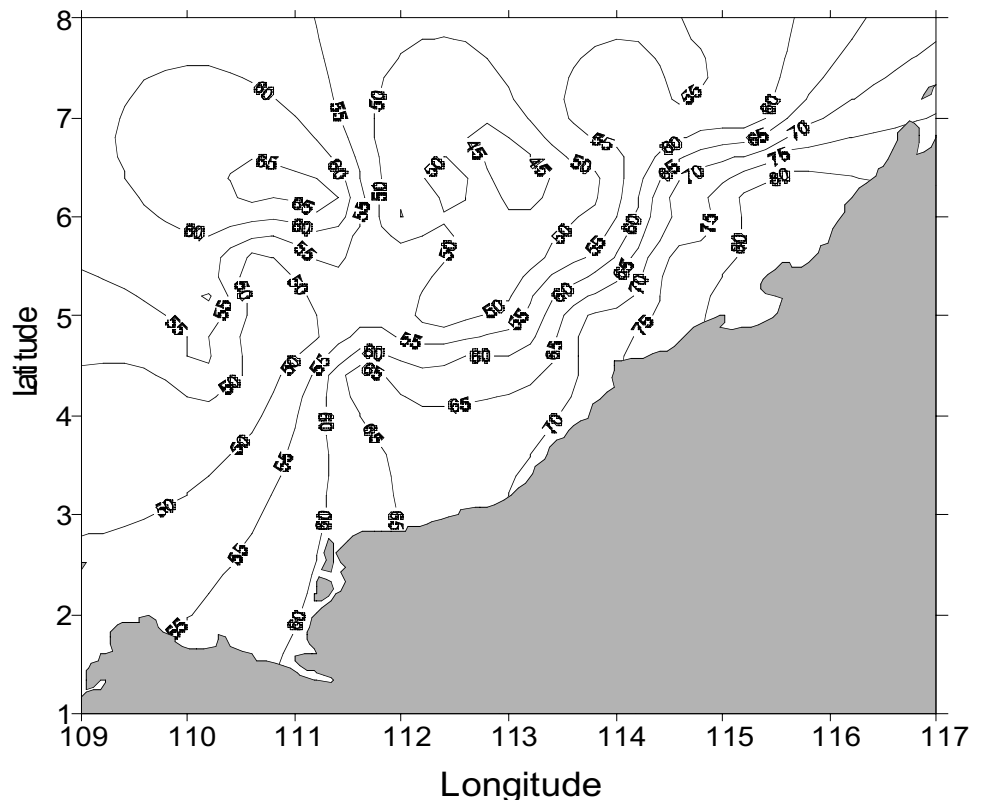
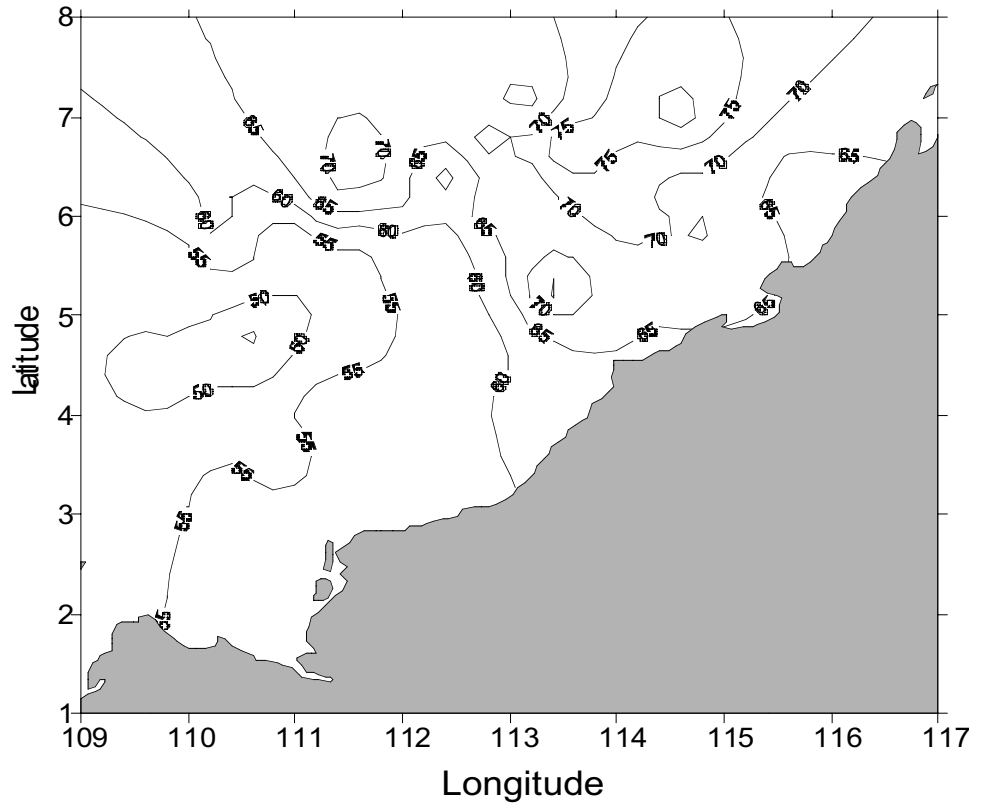


Fig. 11A Depth of 23.0 kg/m<sup>3</sup> sigma theta isopycnal surface (m)

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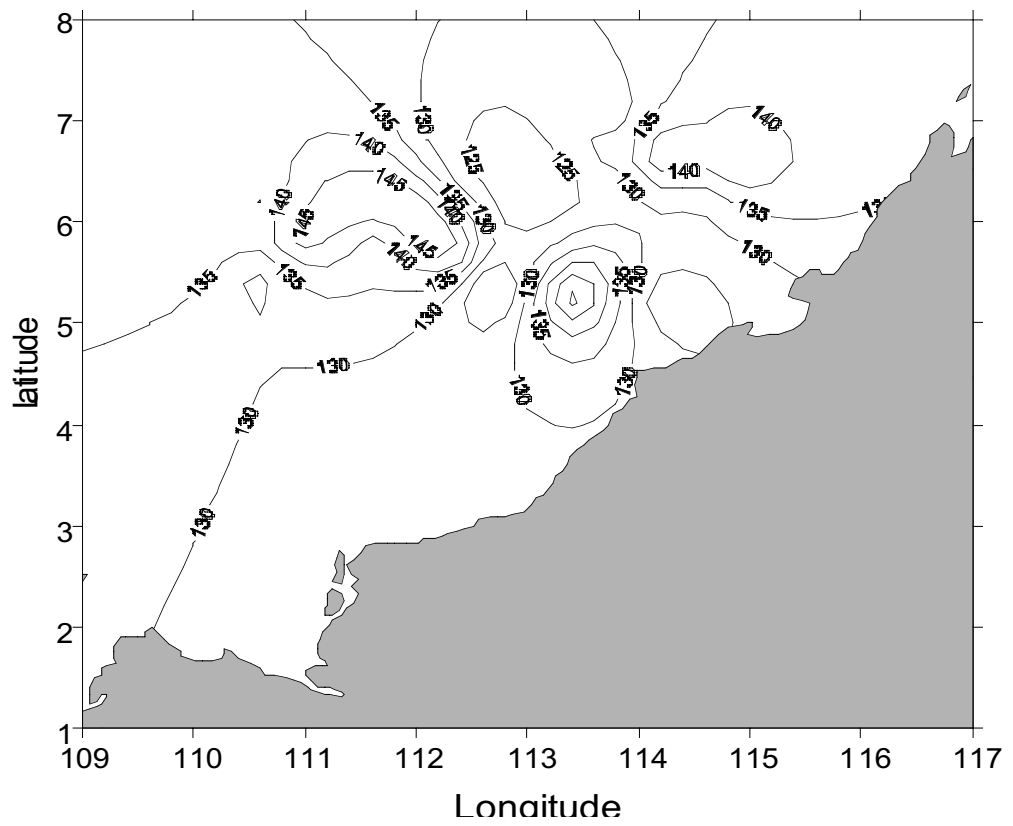
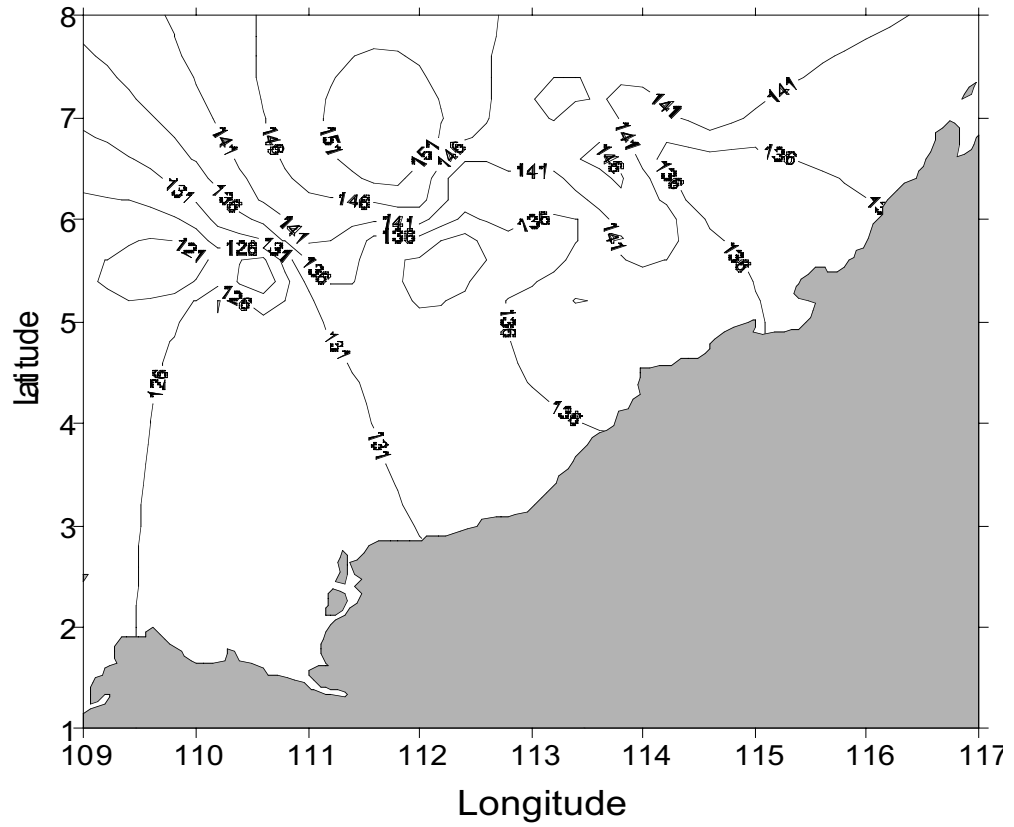


Fig. 11B Depth of 25.0 kg/m<sup>3</sup> sigma theta isopycnal surface (m)

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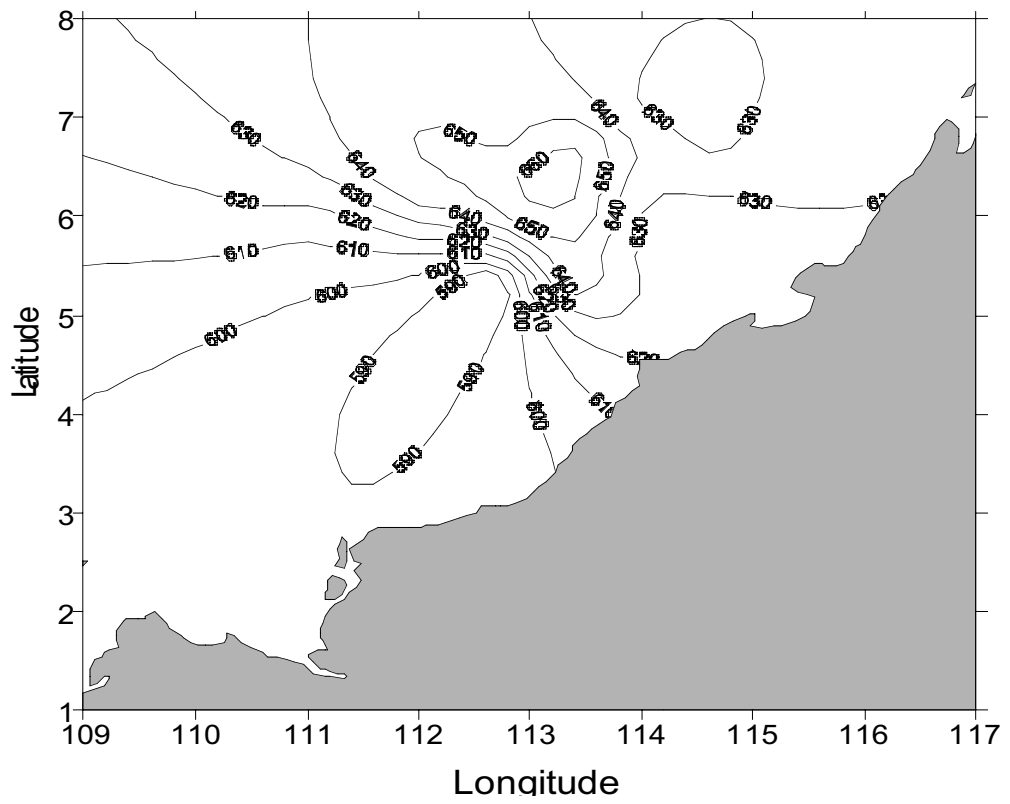
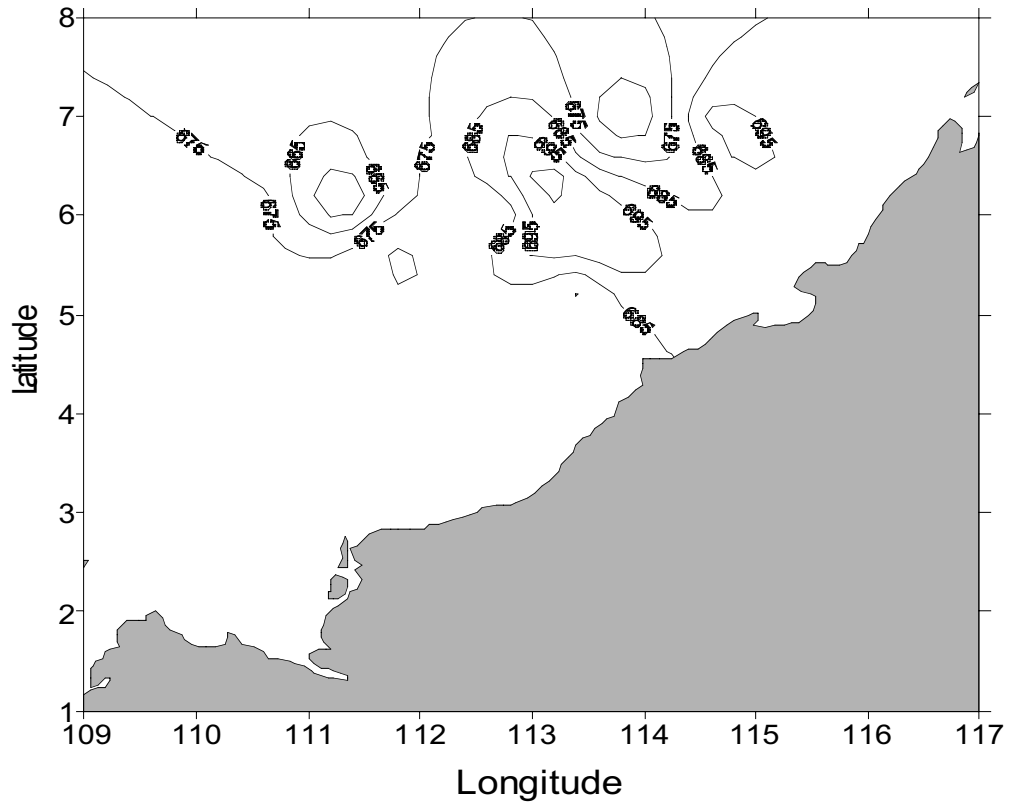


Fig. 11C Depth of 27.0 kg/m<sup>3</sup> sigma theta isopycnal surface (m)



S2/OG4<ANOND>

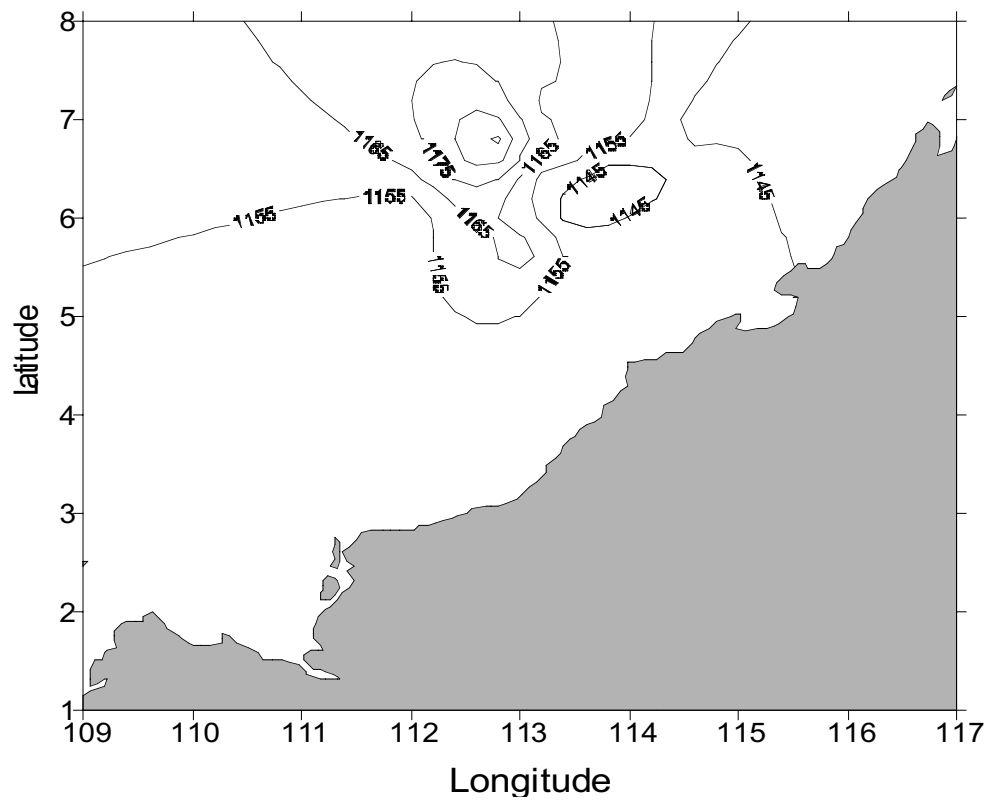
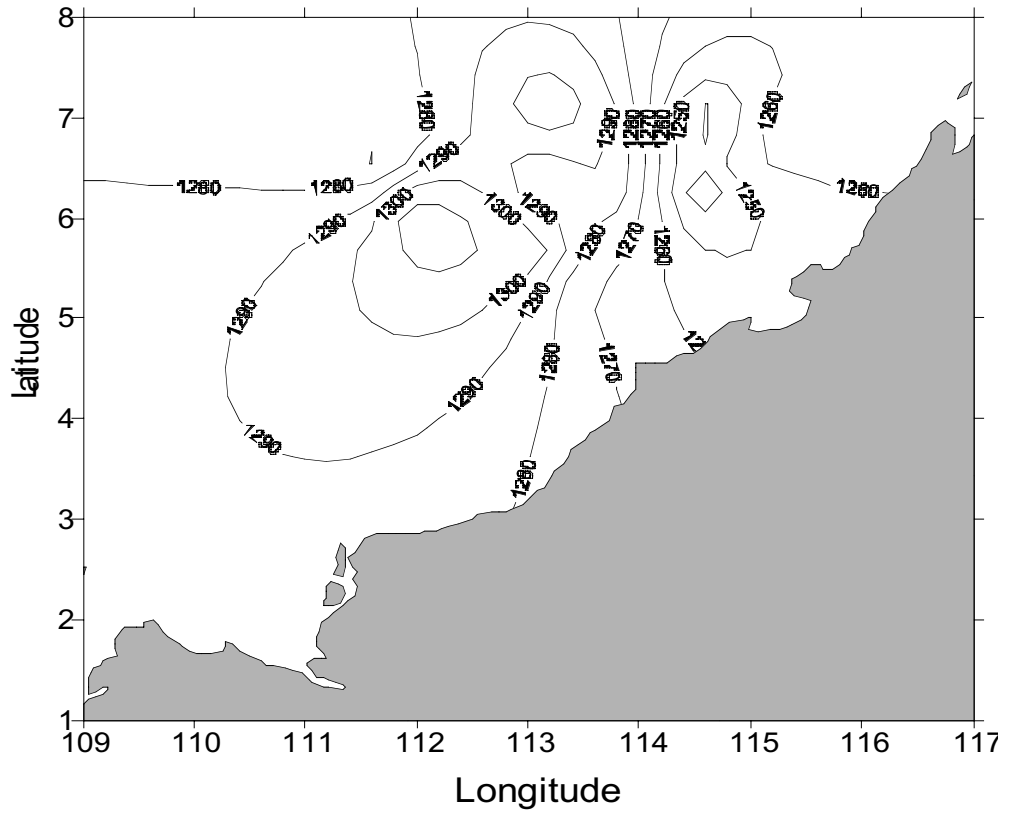


Fig. 11D Depth of  $27.5 \text{ kg/m}^3$  sigma theta