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Three additional layers for Marine Environment Classification: (1) Sea bed temperature; (2) Calcium compensation depth; (3) Sea-bed light levels.

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Three additional layers for Marine Environment Classification: (1) Sea bed temperature; (2) Calcium compensation depth; (3) Sea-bed light levels.

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Executive Summary

Three additional layers were identified as being of potential value in the second phase of the Marine Environment Classification (MEC). This project has brought together experts in physical oceanography, marine chemistry, remote sensing, and underwater optics to produce these three layers:

1. Temperature at the sea bed.
2. Calcium compensation depth or total water depth, whichever is shallower.
3. Light levels (broad-band, photosynthetically active radiation, PAR) at the sea-bed.

Each of these information layers has been produced using long-term average values based on large databases of in situ and remote observations. The values have been remapped onto a Mercator Projection with a mapped average resolution of approximately 1 km. Data are provided for the MEC domain bounded by the following coordinates: 24°–57.5°S 157°E–167°W. Latitude and longitude values for each point in the domain are supplied to facilitate reprojection of the data if required in the future.

The data provided are very close to the cutting-edge of marine research around New Zealand. Being close to research products rather than operational products, there has been, at best, limited validation of the products supplied. Their value within the MEC may become clearer when the second phase of this research is completed.

1. Introduction

The Marine Environment Classification project, co-funded by Ministry for the Environment, Department of Conservation and the Ministry of Fisheries, is designed to define broad patterns in environmental and ecosystem properties in the New Zealand EEZ pelagic and benthic marine environments. The draft MEC design is based on eight environmental variable layers, selected to represent spatial variation in large-scale physical characteristics that ‘drive’ marine ecosystems. Extensive use has been made of numerical models and satellite data to develop factor layers.

The first stage of the Marine Environment Classification scheme was completed in 2005 (Snelder et al. 2005). Three additional layers of information were identified as being useful for developing this work. This project has provided these three data layers for incorporation into the Marine Environment Classification scheme. The project ran from May 2005 to June 2005 and the specific objectives of this work were to provide the following layers:

1. Temperature at the sea bed
2. Calcium compensation depth or total water depth, whichever is shallower.
3. Light levels (broad-band, photosynthetically active radiation, PAR) at the sea-bed.

Each of these data layers represents long-term average values, and aims to be indicative of the climatological average state under existing conditions. The values will be remapped as a Mercator Projection with a mapped average resolution of approximately 1 km. Data will be provided for the marine environment bounded by the following coordinates: 24°–57.5°S 157°E–167°W. Data will be provided as ESRI grid files.

2. Temperature at the Sea-Bed

2.1 Methods

Bottom temperature was calculated by interpolating 3-dimensional, gridded, annual-mean temperature data onto a digital terrain model consisting of 2-dimensional, gridded, topography data. The temperature data was from the World Ocean Atlas 2001 1/4° version 2. This dataset is published by the US National Oceanographic Data Center, see:

http://www.nodc.noaa.gov/OC5/WOA01/qd_ts01.html.

It is constructed by an objective analysis of *in situ* sub-surface ocean measurements, as described by Boyer et al. (2005). The World Ocean Atlas 1/4° grid covers the world oceans at 1/4° spacing in longitude and latitude (as the name implies) and on 33 depths from the surface to 5500 m. The accuracy of the World Ocean Atlas temperature field in the New Zealand region has never been quantified rigorously, but our informal comparisons with other data show that it describes the large-scale ocean features correctly (i.e. on spatial scales of *ca* 200 km or more) but does not capture the finer-scale detail.

The topography dataset was generated at NIWA from depth-contour data. It resembles the one shown in the Undersea New Zealand wall chart (CANZ 1996) but with the addition of extra data in depths shallower than 250 m. The grid is 1 km resolution (Mercator projection, true-scale latitude 46° S). The dataset is an improved version of the topographic data used in the first stage of the MEC.

2.2 Results

The “Temperature at the Sea-Bed” layer is shown in Figure 2.1.

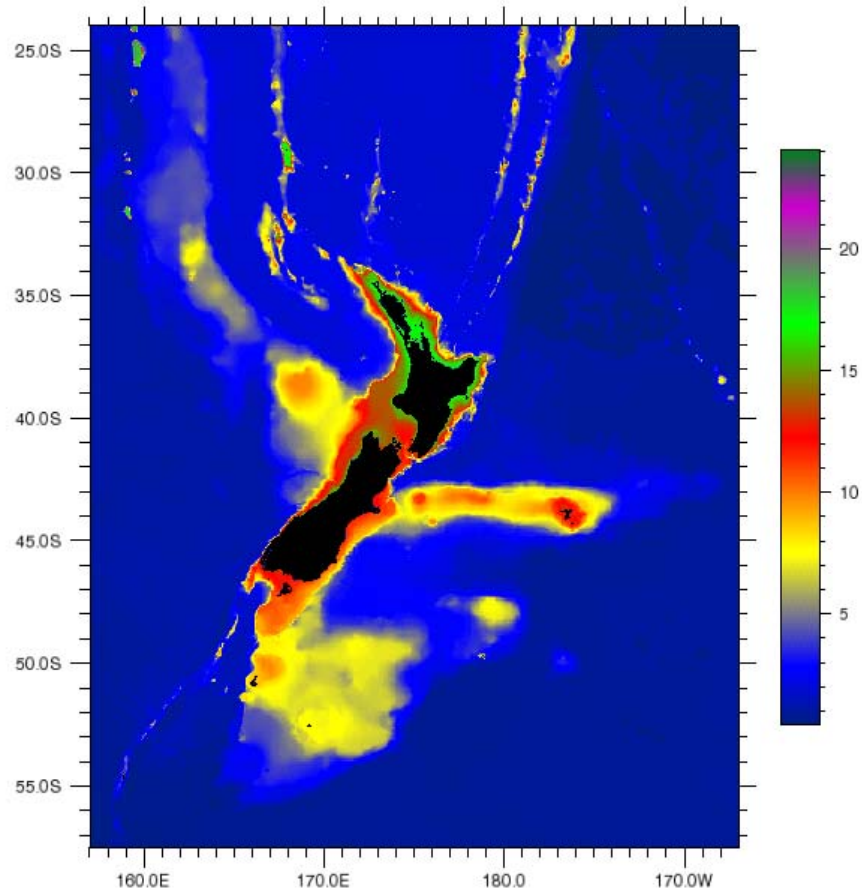


Figure 2.1. Estimated temperature at the sea-bed produced by 3-dimensional interpolation of temperature-depth-location data onto a Mercator projection grid at 1 km resolution.

2.3 Conclusions

The data are qualitatively reasonable, but extensive validation of the data has not been carried out. Validation of the layer would require data within the World Ocean Atlas 2001 to be compared to the NIWA archive of in situ measurements of deep-sea temperature from shipboard CTD measurements. This spatially and temporally extensive validation exercise is not within the scope of the current work.

3. Calcium Compensation Depth

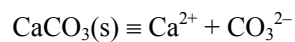
The base data used to produce this layer was provided by Professor Keith A. Hunter, Chemistry Department, University of Otago, Box 56, Dunedin, New Zealand, who is the author of Sections 3.1–3.13 of this report.

3.1 Introduction

The CaCO_3 cycle in the oceans is central to the control of oceanic pH, and thus the CO_2 equilibrium system and atmospheric CO_2 concentration over time scales of 10^3 years. Most of the CaCO_3 formed in the ocean is precipitated in the mixed layer by phytoplankton that are making use of the calcification reaction



to produce both metabolic CO_2 and exoskeletal CaCO_3 . Almost all organisms generate the polymorph *calcite*, although some such as pteropods produce the more soluble form *aragonite*. After grazing by zooplankton, a significant fraction of this CaCO_3 sinks into deep water as biogenic debris and is subject to dissolution. The fate of this biogenic CaCO_3 is well understood in terms of its solubility chemical equilibrium. For the dissolution equilibrium



CaCO_3 depositing on the sea floor will be stable to dissolution if the sea floor lies in a region where the surrounding seawater is supersaturated according to the above equilibrium. This will occur if the ionic product $Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$ exceeds the value of the stoichiometric solubility product constant K'_{sp} for the dissolution reaction. This concept is often expressed in terms of the CaCO_3 saturation index Ω defined as follows:

$$\Omega = \frac{Q}{K'_{sp}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K'_{sp}}$$

Thus for supersaturated water $\Omega > 1$ while for undersaturated water $\Omega < 1$.

This can be further simplified by noting that the concentration of Ca^{2+} in seawater is approximately constant (when normalized to salinity), so for simple considerations it is sufficient to compare the *in situ* $[\text{CO}_3^{2-}]$ with the concentration that would obtain in equilibrium with CaCO_3 . This is illustrated in Figure 3.1 using a typical set of data taken from the South Pacific.

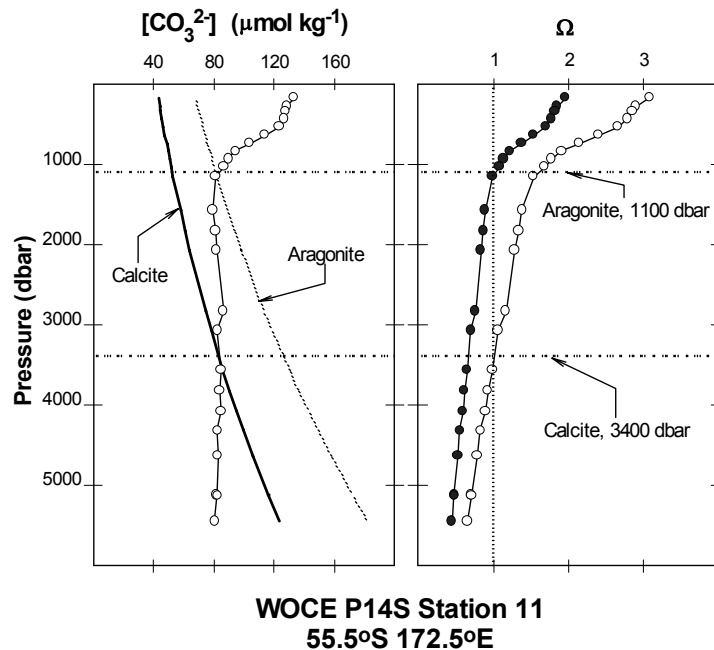


Figure 3.1: Left panel shows *in situ* concentrations of CO_3^{2-} calculated from measurements of C_T and A_T for an example WOCE P14S station, together with the calculated concentrations of CO_3^{2-} in equilibrium with both calcite and aragonite as a function of pressure. Right panel shows the corresponding pressure dependence of the saturation index Ω for each CaCO_3 polymorph.

The left panel shows how the *in situ* $[\text{CO}_3^{2-}]$ and the equilibrium values for calcite and aragonite vary with pressure (i.e. depth). The equilibrium solubility values for both polymorphs increase with depth both because of the effects of pressure on the solubility equilibrium and because of temperature effects (T decreases with depth). The *in situ* $[\text{CO}_3^{2-}]$ decreases with depth because of what is termed the *biological pump*: biogenic debris contains organic matter which undergoes oxidation to CO_2 in deep water, regenerating nutrients and acidifying deep water. For this reason, the pH of the deep ocean is lower than in the mixed layer and consequently the concentration of $[\text{CO}_3^{2-}]$ is also lower.

The curves for *in situ* and equilibrium $[\text{CO}_3^{2-}]$ cross each other at around 1100 dbar for aragonite and 3400 dbar for calcite. This is termed the *saturation depth*, being the depth at which the seawater is exactly saturated with respect to CaCO_3 . The corresponding saturation indices are portrayed in the right panel of Figure 3.1.

The saturation depth varies throughout the global ocean. Since the depth is controlled by the intensity of the biological pump (the equilibrium solubilities are determined only by depth and temperature and vary only slightly around the globe) the saturation depth is shallowest in the North Atlantic and deepest in the North Pacific.

Figure 3.1 shows that at least from the point of view of the thermodynamic solubility, any CaCO_3 that happens to accumulate on the sea floor at depths shallower than the saturation depth will be thermodynamically stable with respect to any subsequent dissolution. On the other hand, CaCO_3 that accumulates on the sea floor in regions deeper than the saturation depth is unstable and subject to dissolution. Whether it *actually* undergoes dissolution depends on a number of other factors. This can be studied using sediment cores in which the intricate biogenic CaCO_3 exoskeleta can be examined for signs of dissolution. Firstly, some finite degree of undersaturation seems to be required to obtain measurable dissolution, and some authors regard $\Omega \sim 0.8$ as a typical threshold for this. In addition, the rate of sedimentation affects dissolution because rapid burial of CaCO_3 by other sediment components, or itself, can slow down equilibration with the surrounding seawater. Finally, the oxidation of organic matter in the sediments can produce lower pore water pH which enhances dissolution.

The existence of a saturation depth for CaCO_3 explains the geographic distribution of this mineral in deep ocean sediments. Essentially, although CaCO_3 is generated in the mixed layer more or less uniformly throughout the ocean, it is only an important component of shallower sediments lying above the horizon at which dissolution begins.

Over the whole ocean, the net fraction of biogenic CaCO_3 which survives dissolution is controlled by the position of the saturation depth. However, the quantity of CaCO_3 thus preserved must stay in long term balance with the supply of Ca^{2+} and HCO_3^- from limestone and other mineral weathering on the continents. Thus the saturation depth is essentially dictated by continental weathering rates and their effect on ocean alkalinity. This in turn controls atmospheric CO_2 . For this reason, the CaCO_3 system in the ocean provides a mechanism that compensates for fluctuations in ocean chemistry at the expense of CO_2 . For example, if we were to dump a large amount of sodium hydroxide into the ocean, its alkalinity would increase, as would the concentration of CO_3^{2-} throughout the water column. In turn, this would lead to a deepening of the saturation depth, leading to additional CaCO_3 preservation and a

consequent lowering of the ocean's alkalinity until the previous balance was again restored.

It can be seen that there are various parameters that describe the CaCO_3 compensation process: the saturation depth already referred to, the depth at which some defined undersaturation ($\Omega \sim 0.8$) occurs, or the depth at which dissolution of calcite in sediments can be seen (lysocline). For the purposes of this report, we are defining the Calcium carbonate Compensation Depth (CCD) in terms of the saturation depth ($\Omega = 1.0$) and also an Estimated Lysocline Depth (ELD) as the depth at which $\Omega = 0.8$ (ELD).

Thus defined, CCD can be calculated from experimental measurements on the CO_2 equilibrium system in seawater. For this it is important to recognize that this equilibrium system involves a number of variables, not all of which are independent of each other. In terms of the actual CO_2 species present in seawater, these are the concentrations of the species $\text{CO}_2(\text{aq})$, HCO_3^- (the most abundant) and CO_3^{2-} (directly relevant to CaCO_3 solubility). In addition, because the ocean is an open system we need to consider the equilibrium fugacity of CO_2 , $f\text{CO}_2$. Finally, because of the acid-base reactions of CO_2 , pH is an important parameter. The concentrations of these species are linked together through a series of equilibria, whose equilibrium constants are a function of temperature, salinity and pressure. This makes for a complex set of equations.

Of the quantities mentioned, only $f\text{CO}_2$ and pH can be measured directly. In particular, the concentration of the CO_2 species, including that of CO_3^{2-} , cannot be directly measured but must be calculated from a knowledge of the aforementioned equilibrium equations. The most useful, but not unique, way to achieve this is to base the calculations on measured values of the total dissolved carbon dioxide C_T (often termed *dissolved inorganic carbon DIC*) and the alkalinity A_T . These starting parameters are advantageous because they are temperature and pressure independent conservative capacity parameters.

3.2 Summary of approach

The approach adopted in this project therefore consisted of firstly using published information to calculate the equilibrium solubility product as a function of temperature, salinity and pressure for any desired station in the geographical grid. This was combined with published measurements of C_T and A_T for vertical profile stations to obtain estimated values of the saturation index Ω as a function of pressure for each station. From these calculations, an algorithm parameterizing the geographical dependence of the CCD (pressure at which $\Omega = 1$) was derived. This was then used in combination with a grid of bathymetric data to produce a map of CCD or bottom depth, whichever is shallower. Such a map indicates the geographical areas in the New Zealand EEZ at which the CaCO_3 compensation mechanism is likely to be operative.

A similar approach was used to calculate the estimated lysocline depth ELD by calculating the pressure (depth) at which $\Omega = 0.8$ for all stations, then fitting this to a polynomial in latitude.

3.3 Data sources

As explained above, to calculate CCD or ELD it is necessary to have vertical profile data containing S, T and two of the CO_2 system parameters, the latter normally being C_T and A_T . Unfortunately there are very few data that meet this requirement for the New Zealand oceanic region. The GEOSECS programme carried out in the 1960's contained a number of stations in this region. However, C_T was measured indirectly on those cruises from the potentiometric titrations used primarily to measure A_T , and this approach was subsequently shown to involve a systematic error resulting mainly from variable liquid junction potentials for the glass electrode used to measure pH during the titrations (Bradshaw & Brewer 1988; Bradshaw et al. 1981).

It was concluded that the only reliable data set is that gathered during the World Ocean Circulation Experiment (WOCE). Of these, WOCE cruises P14S and P15S, which took place in 1996, overlap partly with the NZ oceanic region of interest (Figure 3.2). There are some other relevant WOCE cruises, but the CO_2 data for these have not yet been released. The tendency in large international programmes like WOCE is to avoid the EEZ of particular countries unless they are contributing to the scientific work on the cruise. This highlights the importance of New Zealand generating its own CO_2 system data in the future.

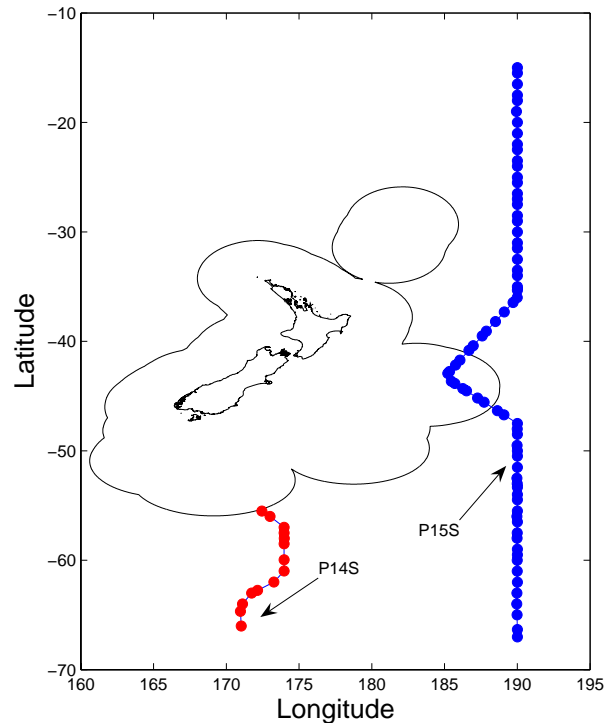


Figure 3.2: Locations of stations on WOCE cruises P14S and P15S in relation to the New Zealand coastline and EEZ.

3.4 Solubility product of calcite

The solubility product of calcite was calculated in a 3-step process involving firstly the thermodynamic value at 1 atm total pressure in pure water as a function of temperature, secondly correcting for the activity coefficient effects of the *in situ* salinity and finally correcting for the *in situ* pressure. This approach was used by Feely *et al* to calculate the CCD in the northeast Pacific (Feely *et al.* 1988).

3.5 Solubility product in pure water

The solubility product of calcite in pure water at 1 atm total pressure, K_{spc}^0 , as a function of absolute temperature T was calculated using the equation given by Millero (1995).

$$\ln K'_{\text{spc},0} = a_0 + a_1T + \frac{a_2}{T} + a_3 \ln T \quad [3.1]$$

where $a_0 = -395.82934$, $a_1 = -0.17959$, $a_2 = 6537.7736$ and $a_3 = 71.595$.

This is based on the thermodynamic formalism of Clark & Glew (1966) and experimental measurements of Mucci (1983).

3.6 Solubility product in seawater at p=0

The dependence of K'_{spc} on salinity in seawater (at 1 atm total pressure) was calculated using the equation reported by Millero (1995) [4]

$$\ln K'_{\text{spc}} - \ln K'_{\text{spc},0} = \left(b_0 + b_1T + \frac{b_2}{T} \right) S^{0.5} + c_0S + d_0S^{1.5} \quad [3.2]$$

where $b_0 = -1.78938$, $b_1 = 0.00655$, $b_2 = 410.64303$, $c_0 = -0.17755$ and $d_0 = 0.0095$. This is again based on measurements of Mucci (1983).

3.7 Effect of pressure on equilibrium constants

Corrections for the effect of pressure on all equilibrium constants were made using equation given by Millero (1979).

$$\ln K'_{\text{spc}}(p) - \ln K'_{\text{spc}}(p=0) = -\frac{\Delta V}{RT} p + \frac{\Delta \kappa}{2RT} p^2 \quad [3.3]$$

where ΔV is the partial molal volume change, $\Delta \kappa$ is the compressibility and p is the gauge pressure. The latter two quantities were parameterized in terms of S and T as follows

$$\Delta V = a_0 + a_1T \quad [3.4]$$

$$\Delta \kappa = b_0 + b_1T \quad [3.5]$$

where $a_0 = -48.76$, $a_1 = 0.5304$, $b_0 = -11.76$ and $b_1 = -0.3692$.

The combined equations [3.1] through [3.5] for calculating the solubility product at any S , T and p were coded as Visual Basic user-defined functions into Microsoft Excel. They were then checked for accuracy against the CO2SYS programme of

Lewis & Wallace (1998). No significant differences were found over the S , T and p range of interest.

3.8 In situ carbonate ion concentration

The *in situ* concentrations of CO_3^{2-} as a function of pressure (depth) were calculated from each of the selected depth profiles in WOCE P14S and P14S cruises for which there were reliable measurements of C_T and A_T down to at least 3500 dbar (the likely location of the CCD). The independent input values were C_T and A_T as discussed earlier. For these input values, it is necessary to solve the chemical equilibrium equations numerically. This was done by varying the concentration of the hydrogen ion $[\text{H}^+]$ as the master variable until agreement was achieved, within a specified numerical precision, between the calculated and actual values of C_T and A_T . The equations for these parameters in terms of $[\text{H}^+]$ and various equilibrium constants were taken from DOE (1994) and conform to the total alkalinity definition of Dickson (1992).

These equations and the numerical solution routines were coded as Visual Basic user-defined functions into Microsoft Excel. They were then checked extensively against the CO2SYS programme of Lewis & Wallace (1998) and the equivalent SWCO₂ software written by the present author (Hunter 1998)

The main issue in terms of the accuracy of these calculations relates to the choice of equilibrium constants for the dissociation of carbonic acid H_2CO_3 , for which there is a number of different experimental value sets. At present there is no universal agreement on which is the best choice of constants, indeed the “best” choice seems to depend on the purpose of the calculations. In this regard, the “best” choice can only be evaluated if the calculated parameter can itself be independently measured, which is the case only for pH and $f\text{CO}_2$ (equilibrium CO_2 fugacity). Since the required parameter in this work, $[\text{CO}_3^{2-}]$, cannot be directly measured, there is no basis for preferring any particular set of constants.

For the present work, I chose the constants reported by Roy et al. (1993) which are the most recently reported and are the default values used by CO2SYS and SWCO₂.

3.9 Geographical grid

A geographical grid spanning the required latitude and longitude range from 24°S to 57°S and from 157°E to 167°W was constructed using grid intervals of 0.5 degree. Because this grid spans 180° longitude, for greater convenience in plotting maps, the longitude was transformed so that all longitudes were regarded as east of Greenwich. This means that any longitude conventionally stated as west of Greenwich is transformed as follows

$$\text{Longitude East} = 360 - \text{Longitude West}$$

All latitudes are south of the equator and were plotted as negative latitudes according to the usual conventions for mapping.

3.10 Bathymetry

The Smith & Sandwell (1997) global bathymetry map (downloaded from Scripps Institute of Oceanography, University of California, http://topex.ucsd.edu/cgi-bin/get_data.cgi) was used to calculate the depth in each grid cell. This is a digital map of the ocean floor, with a horizontal resolution of 1 – 12 km developed by combining data from depth soundings from ships with high-resolution marine gravity data from the Geosat and ERS-1 spacecraft. The values in the database were averaged over the 0.5 degree cells of the grid. Figure 3.3 shows a contour plot of the bathymetry. This bathymetric map shows that most of the EEZ region has a depth shallower than 3500 m which is the expected value of the CCD at these latitudes (see later).