High anthropogenic carbon content in the eastern Mediterranean

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[1] This work presents data of dichlorodifluoromethane (CFC-12), dissolved inorganic carbon and total alkalinity from a cruise to the Mediterranean Sea during October–November 2001, with the main focus on the CFC-12 data and on the eastern basin. Using the transit time distribution method, the anthropogenic carbon concentrations in the basin were estimated. Results were cross-checked with a back-calculation technique. The entire water column of the Mediterranean Sea contains anthropogenic CO_2, with minimum concentrations of 20.5 μmol kg^{-1} (error range: 16.9–27.1 μmol kg^{-1}) in the most eastern part of the basin at intermediate depths, where the waters' mean age is >130 yr. Column inventories of up to 154 mol m^{-2} (132–179 mol m^{-2}) are found and a total inventory of 1.7 Pg (1.3–2.1 Pg) of anthropogenic carbon in the Mediterranean Sea was estimated. There is a net flux of 38 Tg yr^{-1} (30–47 Tg yr^{-1}) of dissolved inorganic carbon through the Strait of Gibraltar into the Atlantic Ocean and an opposite net flux of 3.5 Tg yr^{-1} (−1.8–9.2 Tg yr^{-1}) of anthropogenic carbon into the Mediterranean Sea.

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1. Introduction

[2] The carbon dioxide (CO_2) concentration in the atmosphere has increased from 280 parts per million (ppm) in the preindustrial time period to a present-day value of ~390 ppm. This represents only a fraction of the anthropogenic CO_2 emissions and several attempts have been made to quantify the increase of oceanic carbon inventories. As anthropogenic carbon (C_{ant}) cannot be distinguished directly by measurements from the natural background of dissolved inorganic carbon (C_T), several empirical methods to estimate its concentration have been developed and improved over the past few decades [e.g., *Brewer*, 1978; *Chen and Millero*, 1979; *Wallace*, 1995; *Gruber et al.*, 1996; *Waugh et al.*, 2004; *Touratier and Goyet*, 2004; *Friis et al.*, 2005]. There are significant differences in quantity and distribution of C_{ant} estimated using these different methods [*Tanhua et al.*, 2007; *Alvarez et al.*, 2009; *Vazquez-Rodriguez et al.*, 2009], but generally a consistent picture has emerged. For example, highest C_{ant} column inventories are found in the North Atlantic and estimates for the total C_{ant} inventory in the global oceans in 1994 are 118 ± 19 Pg C, using the ocean tracer-based ΔC^* back-calculation method [*Sabine et al.*, 2004] and 146 Pg C, based on the transit time distribution (TTD) approach [*Waugh et al.*, 2006]. The net CO_2 emissions from 1750–1994 have been estimated to be 283 ± 19 Pg C [*Bindoff et al.*, 2007], thus the two estimates of C_{ant} in the ocean correspond to 42% and 52%, respectively.

[3] The Mediterranean Sea is a marginal sea that has a considerable influence on the circulation in the Atlantic Ocean [*Reid*, 1979; *O'Neil Baringer and Price*, 1997; *Serra and Ambar*, 2002] and which has been suggested to play a relevant role in the drawdown of anthropogenic carbon [*Álvarez et al.*, 2005; *Aït-Ameur and Goyet*, 2006]. It is a semi-enclosed basin connected only to the Atlantic Ocean via the Strait of Gibraltar. The Strait of Sicily, with a water depth of 300–400 m separates the eastern Mediterranean from the western Mediterranean and limits the water exchange between the two basins. The biogeochemistry of, particularly, its eastern basin is strongly influenced by the Black Sea as well as by rivers. The main circulation pattern in the Mediterranean Sea is as follows: Atlantic surface water flows from the Strait of Gibraltar eastward, becoming warmer and saltier. In the Levantine basin, the surface water becomes dense enough in winter to subduct and form the Levantine Intermediate Water (LIW). This returns westwards at depths between 200 and 500 m and leaves the Mediterranean Sea through the Strait of Gibraltar [*Ovchinnikov*, 1984]. In the western and the eastern basins deep water formation takes place in the Gulf of Lyon and the Adriatic Sea, respectively, when cold winds cool the high salinity surface waters [*Gascard*, 1978; *Pollak*, 1951]. The Western and Eastern Mediterranean Deep Waters (WMDW and EMDW) flow near the bottom into the two main basins where they slowly upwell and mix with overlying water. The deep water renewal time has been estimated to be 20–40 years in the western basin [*Stratford et al.*, 1998] and about 100 years in the eastern basin [*Roether et al.*, 1996; *Stratford and Williams*, 1997; *Stratford et al.*, 1998]. After 1989 a new deep water source in the Aegean Sea contributed to form the EMDW and probably increased the upwelling rate greatly [*Roether et al.*,

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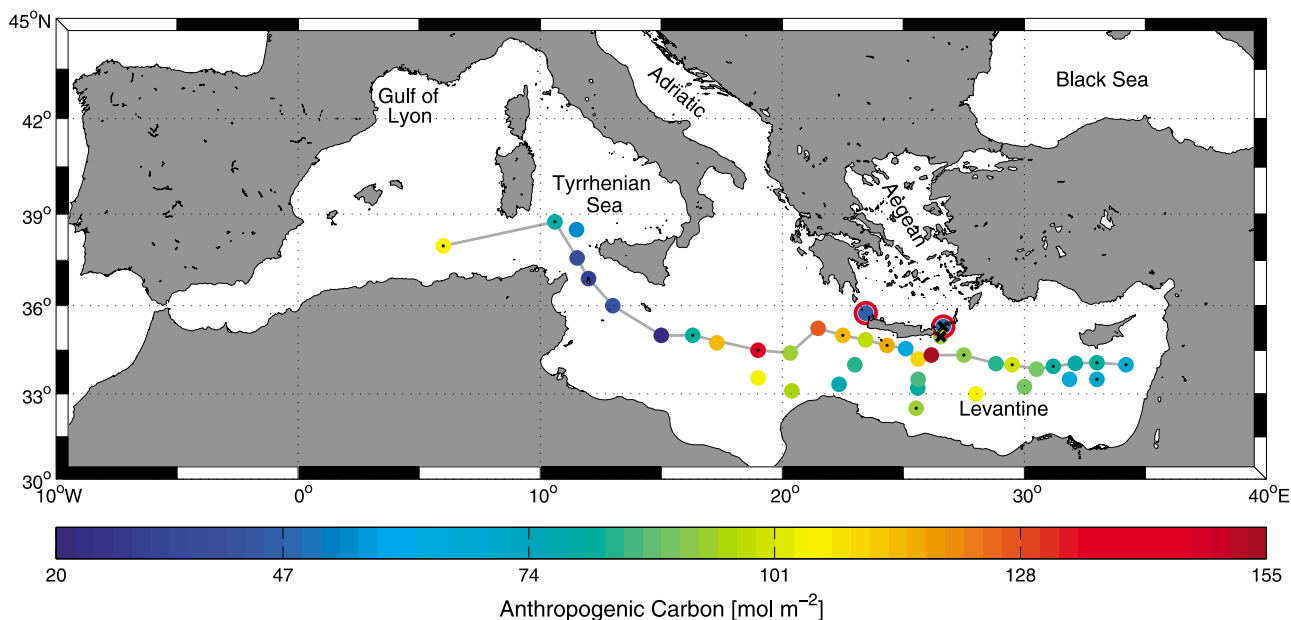
Figure 1. Station plot of the Meteor 51/2 cruise in October/November 2001. Colored dots are the integrated C_{ant} column inventories of all stations in mol m^{-2}. The gray line connects the stations used to create the section plots in Figure 2. The red encircled dots indicate the two stations on the Aegean shelf, which were used to calculate the C_{ant} inventory for the Aegean and the Adriatic Seas. Stations 533 and 534, highlighted with black crosses, are the two stations compared in Figure 3. All stations, where C_T and A_T were measured, are indicated with black dots.

1996]. *Stratford et al.* [1998] suspected a renewal timescale of 30–40 years for recent decades.

[4] Relatively little effort has been made to quantify the C_{ant} content of marginal seas and coastal areas, perhaps because the area of these regions has been considered to be insignificant in terms of C_{ant} uptake compared to the global oceans. In both of the previously mentioned estimates of the global C_{ant} inventory neither data from the Arctic Ocean nor from marginal seas were used. Therefore, in order to obtain a global inventory, an estimate of 12 Pg C for all such regions combined was added by the authors. Since then, the C_{ant} inventory of the Arctic Ocean has been estimated to be 2.1–2.8 Pg C (for the year 1994) by *Tanhua et al.* [2009] which is about 50% less than that estimated by *Sabine et al.* [2004]. Data to assess C_{ant} inventories in marginal seas remain scarce. Until recently there has also been relatively little attention paid to the Mediterranean Sea in terms of its carbon chemistry and, especially in the eastern basin, few reliable data are available. Here we present measurements of C_T and dichlorodifluoromethane (CFC-12), which allow us to estimate the C_{ant} concentrations and inventories and so refine the estimate of the global inventory.

2. Methods

2.1. Water Samples

[5] Between 18 October and 11 November 2001 cruise M51/2 of the R/V Meteor crossed the Mediterranean Sea from west to east. Measurements of salinity, temperature, and oxygen were made at 42 stations along the cruise track. Tracer observations included CFC-11, CFC-12, CFC-113 (SIO 1998 scale), helium isotopes, and tritium at 40 stations. Water for the CFC analysis was sampled first from the 10-L

Niskin bottles to prevent contamination by air and was analyzed directly on board using a gas chromatographic technique described by *Bulsiewicz et al.* [1998]. Data are available from the database CDIAC (http://cdiac.ornl.gov). Here only the CFC-12 depth profiles are examined. The error for the CFC-12 measurements is ±2% or ±0.02 pmol kg^{-1}, whichever is greater. In the following, the CFC-12 data are expressed as "equivalent mixing ratios," which are more descriptive in comparison with temporally varying atmospheric mixing ratios. The equivalent mixing ratio of CFC-12 (in ppt) is obtained by:

$$\text{Equivalent mixing ratio} = \frac{c}{F(T,S) \times [P_{atm} - P_{H_2O}(T,S)]},$$

where c is the CFC-12 concentration in pmol kg^{-1}, $F(T, S)$ is the temperature- and salinity-dependent solubility function in mol kg^{-1} atm^{-1} [*Warner and Weiss*, 1985], P_{atm} is the mean atmospheric pressure in atm, and $P_{H_2O}(T, S)$ is the temperature- and salinity-dependent partial pressure of water vapor [*Weiss and Price*, 1980].

[6] Measurements of total alkalinity (A_T) and C_T were made at 14 stations (Figure 1). Results from alkalinity measurements have been presented by *Schneider et al.* [2007]. Accuracy assessment based on measurements of Certified Reference Material [CRM, supplied by Andrew Dickson, Scripps Institution of Oceanography (SIO), La Jolla, CA, USA] yielded a mean offset of −0.82 ± 2.85 μmol kg^{-1} for A_T and in +0.62 ± 1.01 μmol kg^{-1} for C_T (95% confidence interval, n = 41). Both parameters have been corrected for this mean offset. Precision of the A_T and C_T measurements was 4.2 and 1.5 μmol kg^{-1}, respectively (95% confidence

interval), as determined from duplicate samples ($n = 15$ and $n = 14$).

2.2. Transit Time Distribution

[7] In order to estimate anthropogenic CO$_2$ concentrations, the transit time distribution (TTD) method was applied using the transient tracer CFC-12. The TTD method is based on the idea that each water parcel is composed of different source waters with varying time histories. Each water sample has an age- or transit time distribution. For historical surface water concentrations of CFC-12 the atmospheric time history of *Walker et al.* [2000] was used together with a time-dependent saturation estimated by *Tanhua et al.* [2008]. The latter allows for nonequilibrium surface water concentrations by assuming that the near-surface saturation of CFC-12 was 86% before the year 1989, when the atmospheric growth rate exceeded 15 ppt yr^{-1}, and that it has increased since then, in inverse proportion to its atmospheric growth rate. Since 1999 the saturation is supposed to be 100%. The interior concentration $c(r, t)$ of the tracer at location r and time t is then given by [*Hall and Plumb*, 1994]:

$$c(r,t) = \int_0^\infty c_0(t - t')G(r,t')dt',$$

where t' is the integration variable, representing all the apparent ages in the water parcel (from 0 to ∞ years). $G(r, t')$ is the TTD at location r, giving the appropriate fraction for each water age t' and $c_0(t - t')$ is the surface water tracer concentration in the year $t - t'$ to be multiplied with this fraction. For steady transport the TTD at each interior location can be approximated by an inverse Gaussian function [*Waugh et al.*, 2004], that is:

$$G(t') = \sqrt{\frac{\Gamma^3}{4\pi\Delta^2 t'^3}} \times \exp\left[\frac{-\Gamma(t' - \Gamma)^2}{4\Delta^2 t'}\right],$$

where Γ is the mean transit time ("mean age") and Δ defines the width of the TTD. The Δ/Γ ratio is a measure for mixing. The larger the ratio the stronger the mixing. Here $\Delta/\Gamma = 1$ is assumed, which has been shown to be reasonable for ocean interior waters [*Waugh et al.*, 2004] but has not yet been tested for its applicability to the Mediterranean Sea. Given an interior CFC-12 concentration (or age) and the above approximations, the mean age of the water sample can be constrained. Further, with the help of the atmospheric history of anthropogenic CO$_2$ and an alkalinity-salinity (A_T-S) correlation for this specific area [$A_T = 73.7(\pm 3.0) \times S - 285.7$ (± 114.9) μmol kg^{-1}] [*Schneider et al.*, 2007] the anthropogenic carbon concentration was determined as follows:

$$C_{ant}(t) = \int_0^\infty C_{ant,0}(t - t')G(t')dt',$$

where t is the sampling year. The local variable r can be left out because for each discrete water sample a new TTD is determined.

3. Results

[8] The main focus of this work lies on the eastern basin as only a few stations were sampled in other regions of the Mediterranean Sea. These few data may not be fully representative for the whole basin but all available data have been used in the interpretation, in order to obtain a first estimate of the anthropogenic CO$_2$ inventory of the Mediterranean Sea. A detailed error analysis, including consideration of uncertainties associated with incomplete sample coverage, is provided in section 4.

3.1. Carbon and Tracers

[9] The Mediterranean Sea is known as a basin where remineralization and evaporation dominate. The lowest C_T concentration (2150 μmol kg^{-1}) is found in the upper 100 m with the inflowing Atlantic water and increases toward the east in part due to evaporation (Figure 2). With increasing depth, addition of respiratory CO$_2$ also leads to high C_T concentrations. Below 500 m, in the eastern basin C_T stays rather constant at about 2305 μmol kg^{-1}. In the deep western basin concentrations are slightly higher (up to 2330 μmol kg^{-1}). Estimates found in the literature for the C_T concentration in the inflowing Atlantic water through the Strait of Gibraltar are about 2100 μmol kg^{-1} and for the outflowing Mediterranean water 2300 μmol kg^{-1} [*Copin-Montégut*, 1993; *Santana-Casiano et al.*, 2002; *Aït-Ameur and Goyet*, 2006]. The C_T data presented here are consistent with these values.

[10] Waters in the Mediterranean Sea circulate relatively fast. Residence times in the entire basin have been estimated from a water balance to be ~150 yr (using data of the water volume of the Mediterranean Sea [*Menard and Smith*, 1966] and water inputs from the Atlantic Ocean [*Bryden et al.*, 1994], the Black Sea [*Besiktepe et al.*, 1994], rivers [*Tixeront*, 1969], and precipitation [*Tixeront*, 1969]). It is therefore not surprising that the entire water column in the Mediterranean Sea is found to contain detectable levels of the anthropogenic tracer CFC-12 (Figure 2). CFC-12 in the atmosphere has increased from 0 ppt in the 1930s to a maximum of almost 550 ppt in 2001. Since then concentrations have slowly decreased. With no, or little, atmospheric CFC-12 change per year, the near-surface water and the atmosphere are expected to be close to equilibrium and similar mixing ratios should be found in both phases. Accordingly, the presented CFC-12 data in the surface water from the year 2001 show contemporary high levels of more than 500 ppt, decreasing rapidly with depth to around 200 ppt at 500 m. The lowest concentrations are found between 800 and 1500 m with a value of 71 ppt in the easternmost part of the basin. Below 1500 m the CFC-12 mixing ratios increase again up to 220 ppt near the bottom. This reflects the rapid deep water formation in the marginal seas, which entrains surface water to the deep basins.

[11] The mean ages show the same main features as the tracer concentrations (Figure 2) reflecting the direct dependency of the two parameters. The westward flow of the LIW at 150–400 m, with a renewal timescale of 10–20 yr (determined using a series of tracer experiments based on an eddy-permitting general circulation model of the Mediterranean [*Stratford and Williams*, 1997]), cannot be resolved with these data. In contrast, one can clearly see water at depth with mean ages of 50–60 yr and an old layer between the very young near-surface water and the deep water. The separation of the eastern and the western basins of the Mediterranean Sea at the Strait of Sicily, causes the EMDW
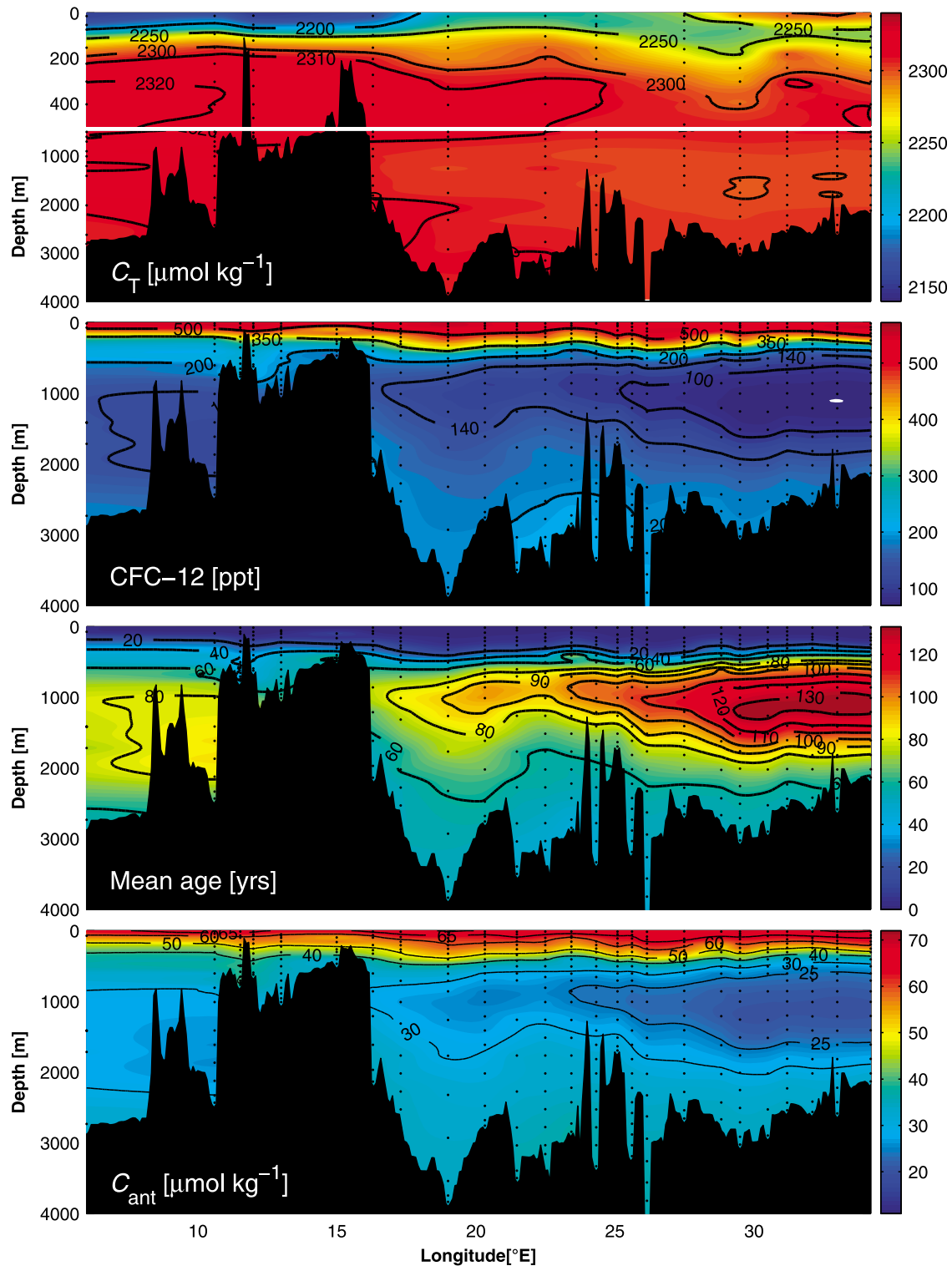
Figure 2. Section plots of the four parameters C_T, CFC-12, mean age, and C_{ant}. The stations used for the section are shown in Figure 1.

to be retained in the eastern basin, where it slowly upwells with a speed of ~35 m yr^{-1} [*Steinfeldt*, 2004] and hence a region of relatively old water with mean ages of more than 130 years can be found around 1200 m.

[12] According to the tracer concentration and the mean age, anthropogenic CO$_2$ has penetrated the entire water column. The upper 500 m are very high in C_{ant} with a maximum concentrations of 70 μmol kg^{-1} (error range: 67–73 μmol kg^{-1}), the EMDW contains ~34 μmol kg^{-1} (error range: 29–39 μmol kg^{-1}) and throughout the basin concentrations always exceed 20 μmol kg^{-1}, even in the easternmost part with the oldest water (Figure 2). Other studies
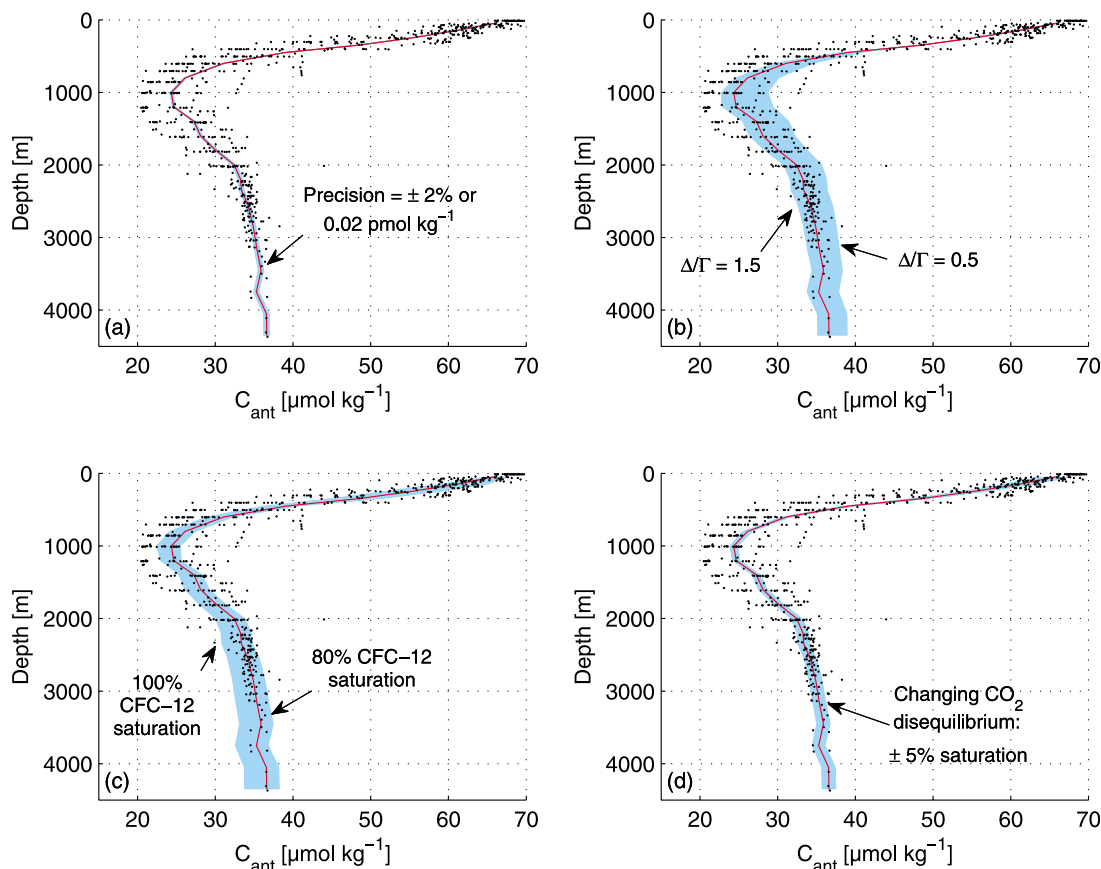
Figure 3. All estimated C_{ant} concentrations (black dots) together with the mean C_{ant} depth profile (red line). Additionally, the error ranges resulting from the maximum and minimum values of several assumptions are plotted (blue shading): (a) uncertainty resulting from analytical precision of ±2% or ±0.02 pmol kg^{-1}, whichever is greater; (b) uncertainty resulting from the maximum and minimum Δ/Γ ratios of 1.5 and 0.5; (c) uncertainty due to the CFC-12 surface water saturation limits of 100% and 80%; (d) uncertainty resulting from a changing CO$_2$ disequilibrium starting with 100% in the year 1900, linearly decreasing and increasing, respectively, by 5% until the year 2000.

of the global oceans show such high concentrations being restricted to depths <2000 m [*Sabine et al.*, 2004; *Touratier et al.*, 2005, 2007; *Tanhua et al.*, 2008]. Consequently, the Mediterranean Sea water column stores large amounts of anthropogenic CO$_2$, which can be explained by its high potential to take up C_{ant} coupled with fast deep water formation in autumn and winter. This is discussed further in section 5.1. Recently published C_{ant} estimates, using the TrOCA method in the Mediterranean Sea show much higher concentrations in the surface water of up to 135 μmol kg^{-1} [*Rivaro et al.*, 2010]. This implies a pCO$_2$ increase of about 200 ppm since preindustrial times, which seems impossible. Also in deeper layers C_{ant} concentrations from *Rivaro et al.* [2010] tend to be higher than our estimates, but increased C_{ant} concentrations in the relatively young WMDW and the EMDW are not seen.

3.2. Anthropogenic CO$_2$ Inventories

[13] Anthropogenic CO$_2$ concentrations were integrated vertically over 50 m layers and linearly interpolated between layers where measurements were missing. The resulting column inventories of C_{ant} (Figure 1) are high relative to those estimated for the remainder of the World Ocean. For

example the maximum observed column inventory was 154 mol m^{-2} (error range: 132–179 mol m^{-2}) (integrated over a depth of 4300 m), which is considerably higher than the maximum column inventories of 90 mol m^{-2} (integrated over ~5000 m) estimated with the TTD method from the GLODAP v1.1 data set in the North Atlantic [*Waugh et al.*, 2006]. However, the mean sampling year for the GLODAP data set is 1994, so the time difference to the data presented here is 7 yr. Assuming linear propagation of C_{ant} over time into the water column, the percentage C_{ant} increase in the atmosphere over this time period can be subtracted from the C_{ant} estimates in the water, resulting in time-corrected column inventories for the Mediterranean Sea for the year 1994. The maximum Mediterranean inventory of C_{ant} would have been 133 mol m^{-2} (error range: 114–154 mol m^{-2}) in the year 1994, which remains ~45% higher than the maximum column inventories estimated by *Waugh et al.* [2006] for the global ocean.

[14] In the open ocean, anthropogenic CO$_2$ concentrations decrease rapidly with depth so that only the upper ocean contributes to the C_{ant} column inventory (nearly 50% of the column inventory is contained within the upper 400 m of the water column [*Sabine et al.*, 2004; *Waugh et al.*, 2006]). In

Table 1. Water Volume, Mean Depth, Anthropogenic CO_2 Inventory and Mass/Volume Ratio of the Eastern Basin and the Entire Mediterranean Sea in the Year 2001 and Adjusted to the Year 1994 for Comparison With the World Ocean in the Year 1994 [*Waugh et al.*, 2006]

	Volume (10^6 km^3)	Mean Depth (m)	C_{ant} (Error Range) (Pg C)	C_{ant}/Volume (Pg C/10^6 km^3)
Eastern Basin	2.22	1680	1.0 (0.7–1.2)	0.44
Mediterranean Sea	3.75	1500	1.7 (1.3–2.1)	0.46
Mediterranean Sea[1994]	3.75	1500	1.5 (1.1–1.8)	0.4
Atlantic/Indic/Pacific[1994]	1332.5	4000	134 (94–121)	0.1

contrast, Mediterranean C_{ant} profiles are characterized by a thick layer of minimum C_{ant} concentrations between 500 and 2000 m with elevated concentrations both above and below, so deep and bottom water also contributes significantly to column inventories. See, for example, the mean C_{ant} depth profile shown in Figure 3.

[15] Based on our data, we have estimated the anthropogenic CO_2 inventory of the entire Mediterranean Sea with the corresponding uncertainty, although we note that only a few stations were occupied outside the eastern basin. The C_{ant} concentrations were averaged over 50 m layers and multiplied by the layer volume, which was calculated from a 5 min Terrain Base bathymetry (2-Minute Gridded Global Relief Data (ETOPO2v2), June 2006). Adding up these layer inventories then gave the total inventory. Our data suggest that the Adriatic Sea and the Aegean Sea have differing C_{ant} profile characteristics, likely related to the direct influence of the deep water formation and the shallow depths. This is discussed further in section 4 and section 5.1. Therefore the C_{ant} inventory for these two basins were determined separately using two stations in the southern Aegean Sea, assuming that these stations reflect the properties of the two basins better than the midbasin profiles. As a result we obtain a total inventory of 1.7 Pg (error range: 1.3–2.1 Pg) of anthropogenic carbon for the Mediterranean Sea in the year 2001 (Table 1). The inventory for the eastern basin only is 1.0 Pg (error range: 0.7–1.2 Pg) of anthropogenic carbon. *Waugh et al.* [2006] estimated a total anthropogenic carbon inventory for the Atlantic, Pacific, and Indian Ocean of 134 Pg C in 1994. Hence, compared to the World Ocean, the Mediterranean Sea only contains 0.3% of the water volume but 1.1% of the C_{ant} (after adjustment of the Mediterranean inventory to the year 1994). The relative fraction (mass/volume) in the Mediterranean Sea is therefore remarkably high compared to the global mean.

3.3. Inorganic Carbon Exchange Through the Strait of Gibraltar

[16] The C_T and the C_{ant} fluxes through the Strait of Gibraltar were estimated on assumption of a two-layer system of inflowing Atlantic surface water and outflowing LIW in the Strait. These fluxes should, however, be viewed with caution, as they do not arise from direct measurements within the Strait and because they are explicitly dependent on the water mass exchange.

[17] We assume that the 100 m depth horizon in the Strait of Gibraltar corresponds to the border between the inflow

and the outflow [*Lafuente et al.*, 2002]. For the flux calculations, mean C_T and C_{ant} concentrations in the respective water masses from our three westernmost stations were used (without those located in the Tyrrhenian Sea). Only the C_T concentrations of the inflowing Atlantic surface water were taken from data collected west of Gibraltar [*Aït-Ameur and Goyet*, 2006]. The water volume transports and the respective C_T and C_{ant} fluxes are summarized in Table 2. We estimate a net flux of 38 Tg C yr^{-1} (error range: 30–47 Tg C yr^{-1}) into the Atlantic Ocean, which agrees with previously estimated fluxes [*Dafner et al.*, 2001; *Aït-Ameur and Goyet*, 2006; *de la Paz et al.*, 2008; *Huertas et al.*, 2009]. However, the net flux of anthropogenic CO_2 is in the opposite direction, 3.5 Tg C yr^{-1} (error range: −1.8–9.2 Tg C yr^{-1}), into the Mediterranean Sea and matches a recently published estimate, based on the ΔC^* method (4.2 Tg C yr^{-1} [*Huertas et al.*, 2009]). As noted earlier, C_{ant} concentrations estimated with the TrOCA method [*Touratier and Goyet*, 2004] were much higher at depth. *Aït-Ameur and Goyet* [2006] assessed the total C_{ant} flux entering the Atlantic at intermediate depths through the Strait of Gibraltar with the TrOCA method and their result is one order of magnitude higher than the estimates based on the TTD and ΔC^* methods. As a result, the *Aït-Ameur and Goyet* [2006] estimate gave a net flux of C_{ant} out of the Mediterranean Sea. This seems implausible, because as long as atmospheric CO_2 concentrations increase, the inflowing surface waters from the Atlantic should always have higher C_{ant} concentrations than deeper outflowing waters, which have not been in contact with the atmosphere for several years. Therefore it appears that the TrOCA method is not well suited for C_{ant} estimation in the Mediterranean Sea.

[18] In order to assess how much anthropogenic CO_2 has been taken up within the Mediterranean basin via air-sea exchange, we estimated the total C_{ant} flux into the Mediterranean Sea through the Strait of Gibraltar since preindustrial times and compared this to our estimate of the total C_{ant} inventory. We assumed a linear relationship between the C_{ant} increase in the atmosphere and the C_{ant} uptake by the Mediterranean Sea. This in turn results in a linear relationship between the C_{ant} increase in the atmosphere and the increase of the net C_{ant} transport through the Strait of Gibraltar (assuming steady state). The historical atmosphere CO_2 mixing ratios were taken from the Law Dome and the

Table 2. Carbon Fluxes Through the Strait of Gibraltar[a]

	Water Volume (Sv)	C_T (Error Range) (Tg C yr^{-1})	C_{ant} (Error Range) (Tg C yr^{-1})
Atlantic inflow	+0.89[b]	+722[c] (721–723)	+21.6[d] (19.3–24.3)
Mediterranean outflow	−0.85[b]	−761[e] (753–768)	−18.1[f] (15.1–21.2)
Net flux	+0.04	−38 (30–47)	+3.5 (−1.8–9.2)

[a]Positive values denote Fluxes into the Mediterranean Sea.
[b]*Huertas et al.* [2009].
[c]Averaged C_T concentrations in the upper 100 m west of Gibraltar from *Aït-Ameur and Goyet* [2006].
[d]Averaged C_{ant} concentrations in the upper 100 m of the three most western stations from this work.
[e]C_T concentrations of the three most western stations from this work, averaged between depths of 100 and 300 m.
[f]C_{ant} concentrations of the three most western stations from this work, averaged between depths of 100 and 300 m.

Mauna Loa data sets. From 1850 to 2001 a total anthropogenic input of 157 Tg C (error range: −85–415 Tg C) through the Strait of Gibraltar was determined. This accounts for almost 10% of the total C_{ant} inventory of the Mediterranean Sea, which means that ~90% must have been taken up directly from the atmosphere within the basin. This percentage seems reasonable, taking into account that the mean residence time of the water in the Mediterranean Sea is about 150 years. *Huertas et al.* [2009] estimated a contemporary uptake of anthropogenic CO$_2$ from the atmosphere of 25 ± 3.4 Tg C yr^{-1} in the Mediterranean Sea. Again, we assumed a linear relationship between the C_{ant} increase in the atmosphere and the increase in the uptake from the atmosphere by the ocean. With the estimate of 25 Tg C yr^{-1} [*Huertas et al.*, 2009], the total C_{ant} uptake from the atmosphere since 1850 then sums up to 1 ± 0.1 Pg C, which is around 60% of our total C_{ant} inventory estimate of the Mediterranean Sea. Considering the different methods, assumptions, and uncertainties, the results appear to be internally consistent.

4. Error Estimation

[19] In addition to the analytical error of ±2% or ±0.02 pmol kg^{-1} in the CFC-12 measurements, the assumptions made for the subsequent calculations of C_{ant} concentrations, inventories, and fluxes lead to further uncertainties in the results which we consider to be systematic errors. To provide an estimate for these uncertainties, all calculations were rerun as follows with realistic maximum and minimum values for each of the assumptions used: (1) a time-dependent CFC-12 saturation in surface waters that implies undersaturation during the period of exponential CFC-12 increase in the atmosphere (starting with 86%) and 100% saturation since 1999, (2) a Δ/Γ ratio of 1 in the TTD calculations, and (3) a constant air-sea pCO$_2$ disequilibrium over time for the TTD approach.

[20] For the error estimation the maximum saturation of CFC-12 in surface waters was assumed to be 100% and the minimum saturation 80%. Maximum and minimum Δ/Γ ratios in the TTD calculations were set to 1.5 and 0.5, respectively. We used the simplest assumption for the air-sea pCO$_2$ disequilibrium over time and assumed that natural sources and sinks of CO$_2$ have remained constant. Increasing CO$_2$ concentrations in the atmosphere then only shift them to a higher level by the additional anthropogenic pCO$_2$ uptake. However, changes in temperature, biology, and biogeochemistry can lead to enhancement or weakening of the natural background sources and sinks. For instance, *Louanchi et al.* [2009] modelled the transformation of the Mediterranean Sea from a net source of 0.62 Tg C yr^{-1} in the 1960 s to a net sink of −1.98 Tg C yr^{-1} in the 1990s. As these changes are hard to predict and are mostly unknown, we do not account for them in detail in our error estimation. The three time-series stations European Station for Time-series in the Ocean, Hawaii Ocean Time-Series, and Bermuda Atlantic Time-series Study, all located in the northern subtropics, show a pCO$_2$ increases indistinguishable from the atmospheric pCO$_2$ increase [*Bindoff et al.*, 2007]. Following this assumes that in general the C_{ant} uptake by the Mediterranean Sea has tracked the CO$_2$ increase in the atmosphere and we apply a ±5% change over time in the CO$_2$

disequilibrium for our error estimation. We assume a linear variation of anthropogenic CO$_2$ saturation starting with 100% in the year 1900 down to 95% and up to 110% in the year 2000, respectively.

[21] To compare the effect of these uncertainties, each is plotted with the mean midbasin C_{ant} depth profile (Figure 3). Figure 4a shows the minimum and maximum errors of the column inventories, which result from the combined uncertainties. In Figure 4b we see the mean C_{ant} profile with the standard deviation, which comprises the regional differences and the analytical error. Most regional variation occurs at depths between ~600 and 1200 m. The crosses in Figure 4b are data from the two stations on the southern Aegean shelf with a maximum depth of about 1000 m (Figure 1) and the circled dots are C_{ant} concentrations from stations in the shallow area around the Strait of Sicily. This leads us to assume that shallow regions in the Mediterranean Sea, in general, show more variability in terms of anthropogenic CO$_2$. Together with the systematic errors we can calculate a total error (Figure 4b). To account for the mapping error in our total C_{ant} inventory estimate and in the flux calculations through the Strait of Gibraltar we use the basin-wide standard deviation together with the systematic errors and propagate the resulting total error (Figure 4b) with all inventory and flux calculations.

5. Discussion

5.1. Anthropogenic CO$_2$ in the Mediterranean Basin

[22] The fast overturning circulation in the Mediterranean Sea has led to an overall invasion of the anthropogenic tracer CFC-12 as well as anthropogenic CO$_2$ in the basin. Our results show that the Mediterranean Sea has taken up a large amount of C_{ant} on both a per-volume and a per-area basis, compared to estimates of the global oceans. Surface pCO$_2$ has been calculated from our A_T and C_T measurements and shows values of 400 ppm and higher throughout the basin, suggesting a net CO$_2$ flux to the atmosphere. Underway pCO$_2$ measurements in June 2005 (personal communication, Tobias Steinhoff) were consistent with this high surface pCO$_2$. With increasing atmospheric CO$_2$ concentrations as a result of human activity, the sea-to-air flux decreases, so a net uptake of C_{ant} takes place. The reason why the per-area-uptake is higher than in other oceanic regions seems to be due to the fast deep water formation processes in the Mediterranean Sea combined with surface water having a relatively low Revelle factor. A low Revelle factor implies that, for a given change in atmospheric CO$_2$, the anthropogenic CO$_2$ concentration in equilibrated surface water will be higher than in waters with a high Revelle factor. Due to the strong temperature dependency of the Revelle factor, lowest values between 8 and 9 are found in the tropics [*Sabine et al.*, 2004], whereas in Antarctic waters, values are as high as 15 and in the North Atlantic about 13. In addition high alkalinity has a lowering effect on the Revelle factor. Hence, Mediterranean water has a Revelle factor between 9 and 10 and therewith a relatively high uptake capacity for C_{ant}.

[23] No samples were collected within the areas of deep water formation, neither in the western nor in the eastern basins. However, the two stations located in the southern part of the Aegean Sea (Figure 1) clearly differ from all
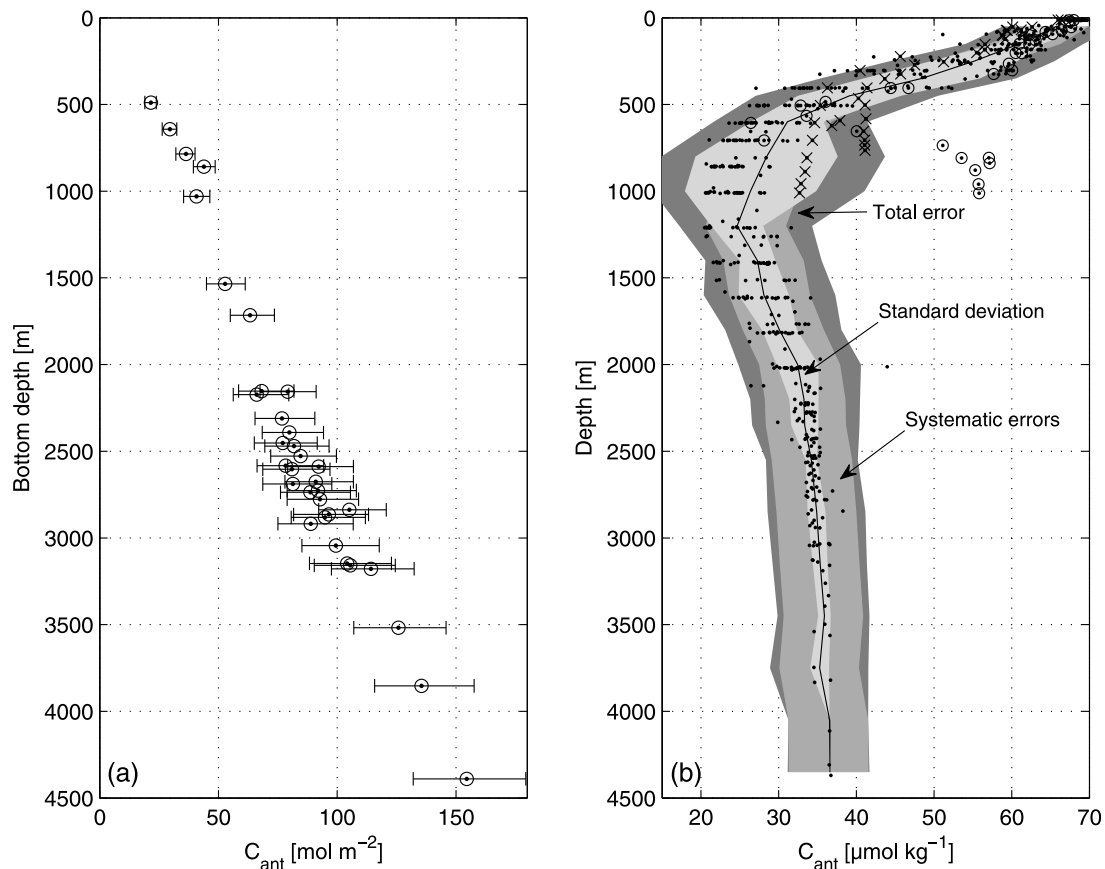
Figure 4. (a) The column inventories in mol m^{-2} with estimated error limits plotted versus the bottom depth. (b) All estimated C_{ant} concentrations and the mean C_{ant} depth profile are plotted together with its standard deviation, which includes the analytical error and the spatial variations (light gray shading), the systematic errors (gray shading), and the resulting total error (dark gray shading). The crosses are data from two stations on the southern Aegean shelf with a maximum depth of about 1000 m (Figure 1), and the encircled dots are C_{ant} concentrations from stations in the shallow area around the Strait of Sicily. The basinwide standard deviation plus the systematic errors were used to calculate the error bounds of the C_{ant} inventory in the Mediterranean Sea and of the fluxes through the Strait of Gibraltar.

other stations and may reflect the properties of that basin. Assuming that these stations are representative for both the Aegean and the Adriatic, we used them to calculate a C_{ant} inventory for these marginal seas. The resulting C_{ant} per volume ratio of 0.63 Pg C/10^6 km^3 is high compared to the remainder of the Mediterranean Sea (0.46 Pg C/10^6 km^3) and to the World Ocean (0.1 Pg C/10^6 km^3), suggesting that these areas might play a major role for the uptake of C_{ant}. In Figure 5, station 534 (Aegean Shelf station) is compared to the closely located station 533 (deep basin station) illustrating the differences in terms of C_{ant} and mean age. Our hypothesis is that in the Aegean and the Adriatic Seas waters with high uptake capacity, which are preconditioned for deep water formation, quickly cool in winter and transfer anthropogenic CO_2 into the deep basin. This scenario could also hold for the Gulf of Lyon.

[24] The C_{ant} estimate for the Aegean and the Adriatic Seas has major uncertainties, both because of the lack of data and by reason of the change in the deep water formation rate in the eastern Mediterranean Sea in the late 1980 s. The so-called Eastern Mediterranean Transient, identified by *Roether et al.* [1996], describes the transition from a
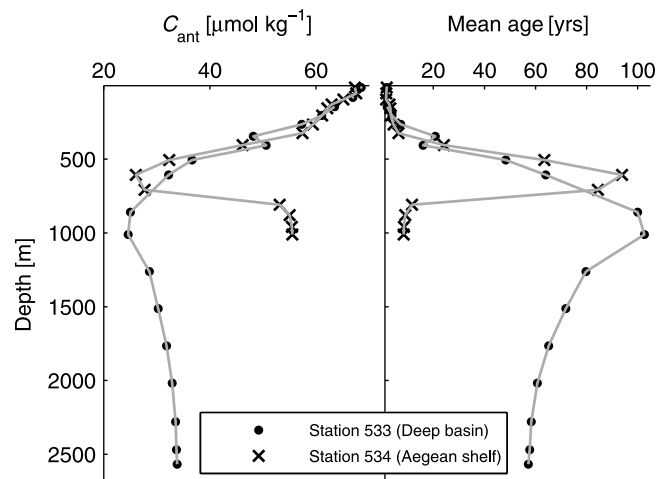

Figure 5. Comparison of the vertical profiles of C_{ant} and mean age at two closely located stations. At station 533 the water depth is more than 2500 m, whereas station 534 is located on the shallower Aegean shelf.
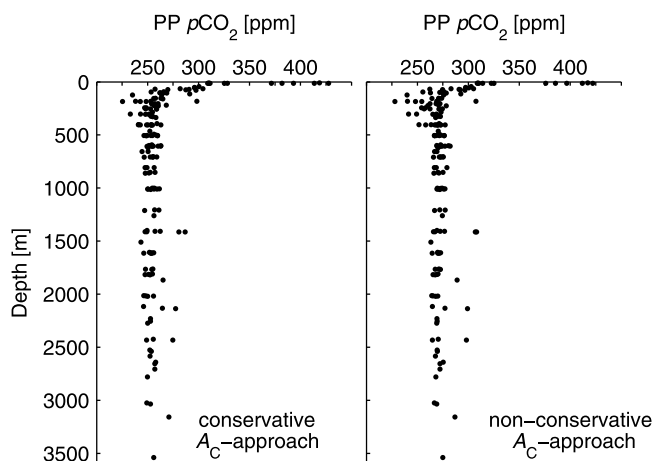
Figure 6. Scatterplot of the preformed preindustrial pCO_2 estimates, determined with (left) the conservative A_C approach and (right) the nonconservative A_C approach.

system with a single source of deep water in the Adriatic to one with an additional source in the Aegean Sea. This additional source only contributes to the deep water formation since about 1990 but with a threefold higher production rate [*Roether et al.*, 1996]. Further studies in 1997 and 1999 [*Theocharis et al.*, 2002] showed that thermohaline deep water formation was still changing at that time and that the eastern Mediterranean Sea was therefore in a transient state. A problem related to this is, that steady state is assumed for the TTD calculations and this assumption must be considered to be of doubtful validity in the year 2001. Thus, future measurements with a second tracer are advised to reduce this uncertainty.

5.2. Preformed Preindustrial pCO_2

[25] There are several methods to estimate the C_{ant} concentration of ocean waters and they are all based on assumptions and have associated uncertainties. In order to cross-check the C_{ant} estimates presented here, obtained with the TTD method, a back-calculation technique was also applied to the carbon and carbon-related data taken during the cruise (C_T, A_T, oxygen, nutrients). For all stations, where C_T had been measured, the preformed preindustrial (PP) pCO_2 was determined. "Preformed" refers to the properties of a water mass at the time when it was last in contact with the atmosphere. Back-calculation approaches attempt to correct properties for all changes that have occurred since the time that a water parcel lost contact with the sea surface. If anthropogenic effects (e.g., elevated atmospheric pCO_2) have influenced the properties, additional correction for these changes result in the "preformed preindustrial" conditions. Accordingly, for each water sample of our profiled stations, the PP pCO_2 is an estimate for the partial pressure of CO_2 the same water mass would have had when it was last at the ocean surface before the period of significant anthropogenic influence.

[26] Two approaches were followed to calculate the PP pCO_2. First, C_T was simply corrected for respiration using the apparent oxygen utilization (AOU) and a C:–O_2 Redfield ratio of 0.76 [*Körtzinger et al.*, 2001]. It was assumed that

the carbonate alkalinity A_C is conservative, that is, there is no carbonate dissolution, because Mediterranean waters are supersaturated throughout the water column with respect to calcite and aragonite [*Schneider et al.*, 2007] (the "conservative A_C approach"). Second, variation of A_C was allowed and C_T was corrected for respiration and for changes due to carbonate dissolution (the "nonconservative A_C approach"). In both approaches the TTD-based estimate of C_{ant} was subtracted, resulting in an estimate of PP C_T. To calculate the PP pCO_2 from PP C_T in the conservative A_C approach the measured alkalinity was corrected for NO_3^- release by biological remineralization. In the nonconservative A_C approach the salinity derived alkalinity was determined from the surface relationship $A_T = 73.7S - 285.7$ μmol kg^{-1} [*Schneider et al.*, 2007]. In both cases it was assumed that A_T has not changed from its preindustrial values. The PP pCO_2 was calculated with the software program CO2SYS [*Lewis and Wallace*, 1998] using the carbonic acid dissociation constants (K_1 and K_2) from *Mehrbach et al.* [1973] as refitted by *Dickson and Millero* [1987] and the dissociation constant for HSO$_4^-$ from *Dickson* [1990]. In Figure 6 the PP pCO_2 of the two approaches is plotted versus depth. Both profiles do not show much variation with depth, indicating that, on the whole, the estimates for C_{ant} and respiration, which both have very different and varying depth profiles, are reliable.

[27] With the nonconservative A_C approach the PP pCO_2 is scattered around 270 ppm, implying that surface waters were almost in equilibrium with atmospheric CO_2 concentrations in the preindustrial period. Looking at the corresponding alkalinities in Figure 7, it becomes apparent that in this case there must be a significant alkalinity addition by carbonate dissolution, especially below 500 m. However, the calcite and aragonite saturation state of the Mediterranean Sea is high throughout the water column, hence carbonate dissolution seems unlikely. Furthermore, a gradual increase of alkalinity with depth would be expected but is not seen.

[28] The conservative A_C approach results in a lower PP pCO_2 around ~250 ppm, implying that surface waters, which feed the deep waters, were undersaturated with respect to CO_2 during the preindustrial period. If this approach were valid, the surface A_T-S correlation used in the nonconservative A_C approach would not apply to the waters that supply the deep waters, and an explanation for the low pCO_2 of ~250 ppm is needed. We note that in the eastern basin, the water below 500 m has its origin in the deep water formation areas of the Adriatic and, since the late 1980s, also of the Aegean Sea. An exchange with the western basin is inhibited by the shallow Strait of Sicily. Hence the preformed surface characteristics of this water body are set in the Adriatic and the Aegean Seas. Compared to surface waters in midbasin, from which the A_T-S relationship was determined, a steeper A_T-S correlation might be expected in these areas, because they are highly influenced by the inflow of rivers and the Black Sea, both carrying high alkalinities [*Schneider et al.*, 2007]. Using such a relationship to determine the preformed alkalinities would shift them closer to the values used in the conservative A_C approach. During deep water formation in autumn and winter, cold winds rapidly cool the high salinity surface waters in the marginal seas and cause pCO_2 to decrease. This very dense water probably
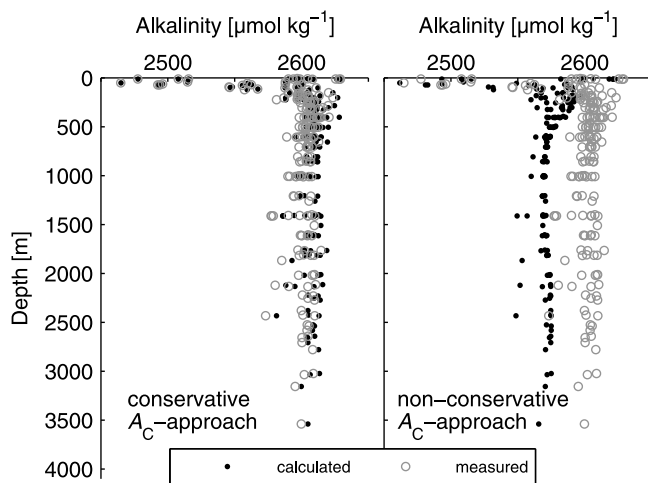
Figure 7. Depth profiles of measured total alkalinity (gray circles) and calculated preformed alkalinity (black dots). (left) The preformed alkalinity was determined from the measured alkalinity by correction for NO_3^- release by biological remineralization, like in the conservative A_C approach. (right) The salinity derived alkalinity, determined from the surface A_T-S relationship, like in the nonconservative A_C approach.

sinks before equilibrium with the atmosphere is reached and a PP pCO_2 of less than 280 ppm could be expected. pCO_2 measurements in the Aegean Sea in February 2006 support this, since the surface waters were undersaturated relative to the contemporary atmosphere [*Krasakopoulou et al.*, 2009]. For these reasons, the conservative A_C approach is favored over the the nonconservative A_C approach and the resulting estimates of preindustrial preformed pCO_2 appear to be reasonable, which in turn suggests that our TTD-based estimates of C_{ant} are accurate.

6. Conclusions

[29] The results presented here show that substantial anthropogenic carbon is present throughout the water column over the entire Mediterranean Sea. The column inventories with a maximum of 154 mol m^{-2} (error range: 132–179 mol m^{-2}) are high compared to those in other areas of the World Ocean. The total inventory of 1.7 Pg of anthropogenic carbon has an error range of at least 1.3–2.1 Pg C. We estimate that there is a net flux of anthropogenic carbon through the Strait of Gibraltar into the Mediterranean Sea of 3.5 Tg C yr^{-1} (error range: −1.8–9.2 Tg C yr^{-1}) but that about 90% of the total C_{ant} inventory in the basin has been taken up directly from the atmosphere via gas exchange. Nevertheless, the Mediterranean is a source of anthropogenic CO$_2$ for intermediate depths in the Atlantic Ocean, since the dense water formed in the Mediterranean Sea spills out of the Strait of Gibraltar and transports C_{ant} to depth and, as noted by *Álvarez et al.* [2005], this entrains additional C_{ant} from central Atlantic waters. To reduce the mapping error associated with the basinwide extrapolation and the flux estimates, tracer measurements in the areas where no samples have been taken are needed, especially in

the marginal seas, in the western basin and in the Strait of Gibraltar. Measurements of a second tracer (e.g., SF$_6$) are important in order to constrain the Δ/Γ ratio and therewith to reduce the uncertainty in the TTD method. Furthermore, knowledge about the saturation state of CFC-12 in areas where the water subducts (Gulf of Lyon, Adriatic Sea, Aegean Sea, Levantine basin) would help to reduce the errors in the age calculations. The effect of changing deep water mass formation over the past 20 years implies that a repeat survey of C_{ant} in the basin is required to validate assumptions of the TTD approach. Despite the uncertainties and assumptions the results of the back-calculated PP pCO_2 with the conservative A_C approach suggest that the TTD method gives a reasonable estimate for the C_{ant} concentrations. Further measurements of alkalinity in the marginal seas are necessary, however, to confirm the hypothesis that the surface relationship between salinity and alkalinity is steeper in the deep water formation areas than in midbasin and the implication that no carbonate dissolution takes place in the Mediterranean Sea.

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